FIELD MUSEUM OF NATURAL HISTORY

PUBLICATION 238

BOTANICAL SERIES VOL. VI, No. 1

CITRUS PRODUCTS

PART I

BY

JAMES B. McNAIR

Associate in Economic Botany

B. E. DAHLGREN

Acting Curator, Department of Botany

EDITOR

CHICAGO, U. S. A.

August 19, 1926

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CITRUS PRODUCTS

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A FLORIDA VALENCIA ORANGE TREE IN BLOSSOM AND FRUIT.

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PREFACE

The literature dealing with citrus products and by-products is extensive but scattered over a wide range of journals, technical and consular reports, and other publications and is often difficult of access. In providing a general account of citrus products, their technology and economics, the author has, therefore, thought it desirable to supplement his own observations and the results of his own investigations with a comprehensive summary of all the principal information available on the subject with the purpose of providing a work of reference useful to those concerned with the citrus industry in its various branches.

This book is divided into two parts. In the first, consisting of ten chapters, descriptions are given of the citrus products from various parts of the plant, such as the entire fruit, the rind, the pulp, the juice, the stem, the leaves, and the flowers. Methods of their manufacture, analysis, and use are also included. The second part deals with methods of production of citrus products in various countries and the economics of the industry.

The term "citrus products," as used here, applies to all products of citrus plants, such as citric acid, essential oil, fruit juice, etc. The term "citrus by-products" refers to by-products of the citrus fruit-growing industry. From an economic point of view, many citrus products are considered as by-products, while others, such as oils of Neroli and bergamot, can in no sense be regarded as such.

In a work of this character, including data from so many sources, individual acknowledgments can not be made. The writer is indebted to various publishers and authors for illustrations, as indicated in each instance. Plate VI and the lower half of Plate V were donated to the author by the La Salle Engraving Co. For references to the numerous sources of information the reader is referred to the bibliography at the end of each chapter and to the author index.

The writer acknowledges gratefully his indebtedness to Dr. B. E. Dahlgren for critical reading and revision of the manuscript. He also wishes to express his appreciation to Miss Mary D. Alexander, who prepared the manuscript for the printer and read the proof.

James B. McNair

Field Museum of Natural History

April 30, 1925

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BOTANICAL CLASSIFICATION OF SPECIES CITED IN THIS WORK[1]

CITRUS L.

C. aurantifolia (Christm.) Swingle *(Limonia aurantifolia* Christm. *Citrus lima* Lunan, not Aitch. *C. limetta* Auth., not Risso). LIME.

C. Aurantium L. *(C. Bigardia* Risso). SOUR or SEVILLE ORANGE.

C. Bergamia Risso. BERGAMOT.

C. Limetta Risso. LIMETTE.

C. Limonia Osbeck *(C. Limonium* Risso). LEMON.

C. maxima Merr. *(C. grandis* Osbeck. *C. decumana* L.). GRAPEFRUIT. Shaddock. Pomelo.

C. medica L. CITRON.

C. mitis Blanco. CALAMONDIN ORANGE.

C. nobilis Lour., var. **deliciosa** (Tenore) Swingle *(C. deliciosa* Tenore). MANDARIN and TANGARINE ORANGES.

C. nobilis Lour., var. **Unshiu** Swingle. UNSHIU or SATSUMA ORANGE.

C. sinensis (L.) Osbeck *(C. Aurantium,* var. *sinensis* L.). ORANGE.

C. taitensis Risso. OTAHEITE ORANGE.

FORTUNELLA Swingle. Kumquat.

F. margarita (Lour.) Swingle *(Citrus margarita* Lour.). OVAL KUMQUAT.

F. japonica (Thunb.) Swingle *(Citrus japonica* Thunb.). ROUND KUMQUAT.

CITROPSIS Swingle and Kellerm. CHERRY ORANGE.

C. Schweinfurthii (Engler) Swingle and Kellerm. *(Limonia Schweinfurthii* Engler).

PONCIRUS Raf.

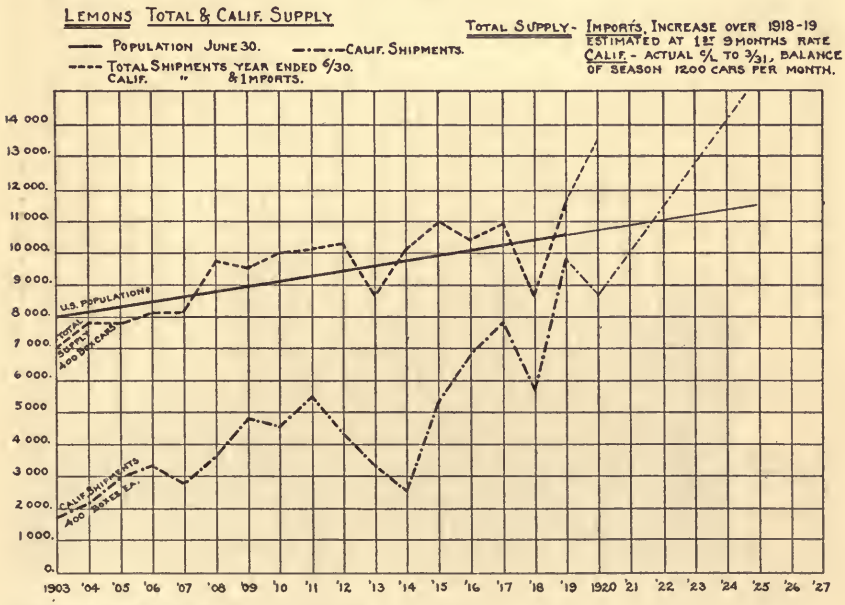
P. trifoliata (L.) Raf. *(Citrus trifoliata* L.). TRIFOLIATE ORANGE.

[1]L. H. Bailey, *Manual of Cultivated Plants.* New York: Macmillan Co., 1924.

CHAPTER I

CITRUS PRODUCTION AND THE CITRUS PRODUCTS INDUSTRY

Citrus fruit growing is an industry of relatively recent development in the United States. Confined by limitations of winter temperature, soil and moisture conditions to a comparatively small area, there is still considerable acreage available for further expansion which appears to be rapidly taking place. Groves planted some years ago are gradually reaching a stage of greater yield, thousands of acres planted within recent years are coming into bearing and thousands of acres are being planted annually. There is thus a tendency to large production which, especially in view of the generally perishable nature of citrus fruits, eventually threatens to amount to an overproduction of fruit for shipment.

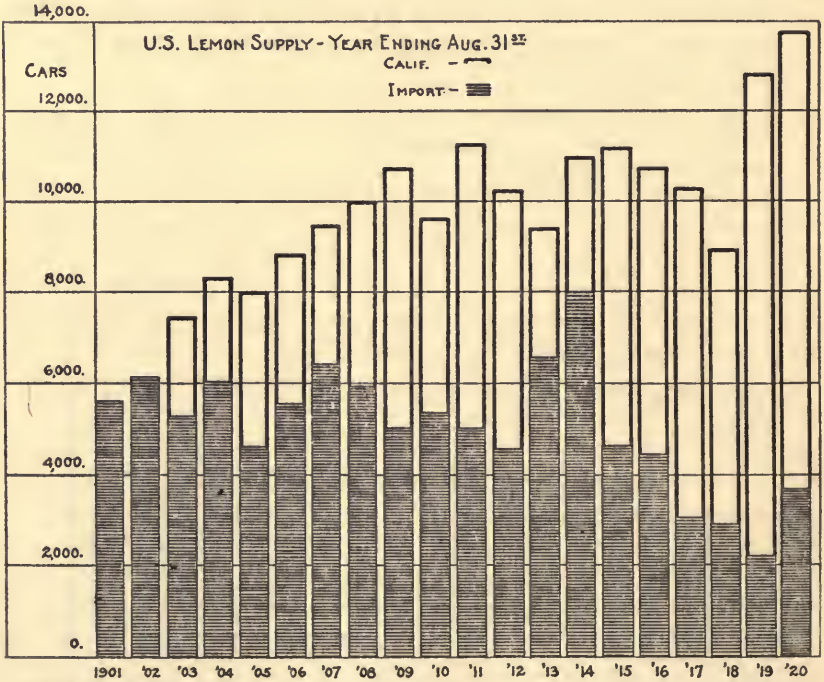

LEMONS TOTAL & CALIF. SUPPLY
POPULATION JUNE 30.
CALIF. SHIPMENTS.
TOTAL SHIPMENTS YEAR ENDED 6/30.
CALIF. " & IMPORTS.
TOTAL SUPPLY- IMPORTS, INCREASE OVER 1918-19 ESTIMATED AT 1ST 9 MONTHS RATE
CALIF. - ACTUAL 6/1 TO 3/31, BALANCE OF SEASON 1200 CARS PER MONTH.
14 000
13 000.
12 000.
11 000.
10 000.
9 000.
8 000.
7 000.
6 000.
5000
4 000.
3 000
2 000.
1 000.
0.
U.S. POPULATION
TOTAL SUPPLY 1903 4000 BOX CARS
CALIF. SHIPMENTS 1903 2000 BOX CARS
1903 '04 '05 '06 '07 '08 '09 '10 '11 '12 '13 '14 '15 '16 '17 '18 '19 1920 '21 '22 '23 '24 '25 '26 '27

(California Citrograph)

FIG. 1.—Total and California supply of lemons, 1903–20. While California has secured a larger share of the American lemon market, the total supply has increased only in proportion to population. From now on, there must be a very rapid increase in per capita consumption to absorb an anticipated increase in California shipments of 60 per cent in five years.

An analysis of, e.g., the consumption of lemons in the United States shows that it increased one-half in ten years. While the quantity imported remained nearly constant during this period, the domestic production doubled. In 1903 California furnished approximately one-fourth, in 1912, one-half, in 1918, four-fifths, and today produces an amount of lemons equal to the consumption in this country. This local increase in production will continue. In 1918, the lemon shipments consisted of 6,913 cars, in 1923 of 8,430 cars. A similar condition exists in the orange industry; 28,444 cars were shipped in 1918, and 71,971 in 1923.

Economic conditions in this field will undoubtedly become serious as the market price of the fruit diminishes and the cost of production increases. The situation may be ameliorated by converting present waste fruit into marketable products and by securing a profitable use for surplus fruit.



(California Citrograph)

FIG. 2.—Total consumption of lemons in the United States by years, 1901–20. Carloads are figured on a 380-box basis, and imports from Sicily are transposed into a carload equivalent. It will be noted that in general imports have decreased in proportion as California shipments have increased with the exception of crop-failure years for California. The substantial increase in total consumption during the last two years is shown by the columns at the right.

In this connection it is of interest to note that in the Mediterranean region the bergamot is grown especially for the essential oil of its fruit and some other citrus trees for the oil of their flowers. In Sicily approximately one-third of the lemon crop is made into citrate of lime, lemon oil, and other "by-products." It is not surprising, then, that a citrus products industry is beginning to become established in the United States.

Outside of southern California, the lemon-growing industry is almost entirely confined at present to southern Italy and Sicily, where the fruit-growing industry is conducted at a disadvantage because of the large amount of hand labor required in orchard care. For frost protection during the winter months the citrus trees there are covered with straw mats fastened to trellises which are removed when the danger of frost is past. The terraced arrangement of the groves also calls for much more care in irrigation and in cultivation than do the groves in the United States. The economic position of the proprietors of the orchards along much of the coast from Naples southward to Salerno is now unsound, because of the large emigration of laborers from this coast to America and the consequent rise of wages. Only with cheap labor could the terraces there have been built at a profit to the landowner, and only with cheap labor is their cultivation now practicable.

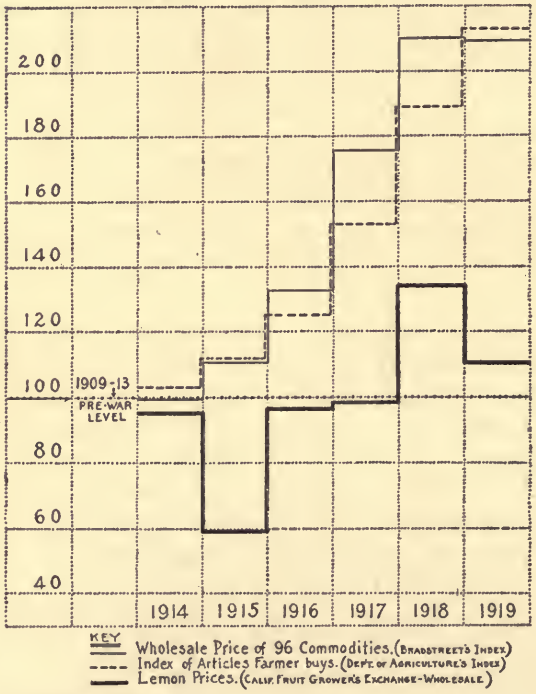
Though fruit not suitable for exportation from Italy and Sicily is usually converted into citrus products, various circumstances, such as price of labor, cost of transportation, and the financial condition of the operator, affect the decision as to whether a crop otherwise exported is to be so manufactured. Less capital is required to export the fruit, but it is cheaper to transport citrate and oil to market. The citrus products industry is profitable, but is still in a rather crude condition, as machinery, where used at all, is mostly primitive. Since after the war with Germany economic conditions have been worse and labor costs higher, good machinery is, however, being sought to take the place of hand labor.

The citrus products industry has the same relation to lemon and orange production as the drying and canning industries have to other fruit-growing. To the citrus fruit-grower it affords a means of utilization of waste fruit, a better price for low-grade fruit, and a market for the crop during periods of low prices.

CITRUS WASTE PRODUCTS

The largest item of waste in the citrus fruit industry is waste or cull fruit. Estimates of the amount of cull fruit in California vary

from 1 to 5 per cent of the fruit shipped or about 25,000 tons per year. Culls may be classified as follows: (1) fruit which shows physical injury on the rind such that it is susceptible to rapid mold growth and decay; (2) decayed and partially decayed fruit; (3) fruit which is defective in shape, or has blemishes (*Euthrip* scars, red spider marks, etc.) which are not a source of attack for molds and fungi, but which injure its appearance and therefore give the fruit a low market value; (4) frozen and sunburned fruit. Lemons which have partially decayed are still valuable as a source of citric acid. Undecayed fruit may be used for marmalade, citric acid (except oranges and grapefruit), juice, oil, peel, or other products.

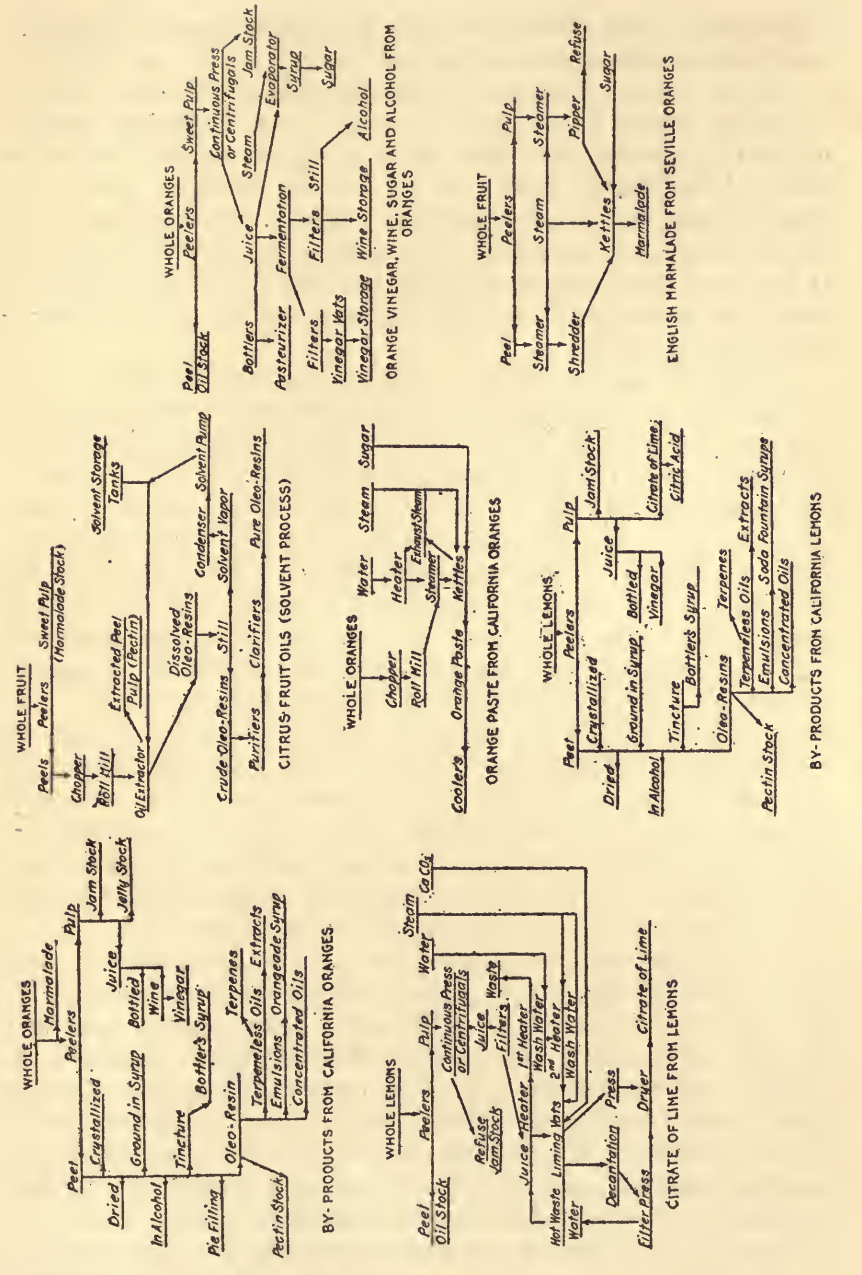


(California Citrograph)

FIG. 3.—Wholesale lemon prices compared with prices of other commodities, 1914-19.

As regards the utility of frozen lemons Chace finds that those which have been very badly frozen are still available for making citrate of lime or citric acid. If the fruit has been thawed gradually enough, little or no permanent injury occurs; but if thawing is rapid, death of tissue takes place. The effect of frost on the fruit is quite similar to sunburn. The killed tissues allow the moisture to evaporate and as a consequence the fruit shrivels.

Where drying has taken place, the yield may be somewhat lowered, but in most cases a fair recovery can be made. Thomas, Young, and Smith, in their paper upon the composition of frozen oranges, and lemons recently published in the *University of California Bulletin No. 304*, show that even two months after the freeze of 1913, frozen lemons contained as high as 4.79 per cent of anhydrous citric acid in the juice.



(R. T. Will: Jour. Ind. and Eng. Chem.)

FIG. 4.—Typical flow sheets illustrating various citrus by-products industries

With many frozen lemons, however, decomposition is rapid and the sooner they reach the factory the better.

So far as oil is concerned, experience shows that, where there is no serious surface injury, the oil content is not diminished, and the oil itself is somewhat more easily recovered than in the case of unfrozen fruit. Where surface injury has not been too great, the peel can be used for candying, drying, or packing in brine. Where the pulp is not injured in flavor, it is available for use in marmalade. Past experience in Florida on grapefruit should teach great caution, however, in bottling juice from frosted fruit, even where it apparently is of excellent quality at the time of bottling.

Oranges, frozen or unfrozen, are not available for the manufacture of citric acid or citrate of lime as the acid content of the juice is not sufficient to pay for its recovery. If the surface injury is not great, the oil recovery will not be curtailed, and surface injury, with oranges, is not usually serious. Candied, dried, and brined peel can be produced from the rinds. The pulp also is available for use in marmalade. As shown by Thomas, Young, and Smith, there is a loss of sugar in the juice of frozen oranges, and our experience is that the loss of flavor is considerable, so that the material has been lessened in value as marmalade stock, although the pectin in the peel, which is valuable on account of its jellying properties, does not seem to decrease greatly.

Where the fruit has not dried out to too great an extent, it can be used for vinegar-making; loss of sugar in the juice, however, lessens its value as vinegar material. It is not possible to produce even with the roller process a standard vinegar where the juice contains less than 8½ per cent of sugar. With rapid-process generators, the content must be even higher. The bitter flavor, sometimes present in the juice from frozen fruit, does not seem to affect the vinegar made from it.

Aside from satsumas, grapefruit is probably more frost resistant than any of the other citrus fruits commonly grown. Its uses in by-products, however, are limited. Citric acid is not present in its juice in sufficient quantity to make its recovery profitable. It contains an insufficient amount of sugar to make a standard vinegar, and while the juice can be satisfactorily bottled, it is best not to use frozen material in its preparation. The peel from frozen grapefruit is satisfactory for the preparation of candied peel, and there is no reason why the pulp cannot be used as usual in the preparation of marmalade.

Cull fruit is the most important source for manufactured citrus products and is the one most generally considered. Orange flowers have been used in the manufacture of the essence of neroli since the

sixteenth century. Orange and lemon flowers are also used in the manufacture of pomades and perfumes. Stems and leaves are used in the manufacture of essential oils, and orange leaves contain a soporific substance.

EQUIPMENT OF CITRUS PRODUCTS FACTORIES

Citrus product factories in the United States, where the cost of labor is high, must rely upon machinery for the carrying on of successful competition with low-priced foreign products.

For the manufacture of citric acid, a crusher, fermentation tanks, filter-press, neutralizing and decomposing tanks, evaporating tanks, vacuum pan, and crystallizing tanks are necessary. The initial outlay for equipment in this process is quite heavy.

Oil production likewise requires a heavy expense for machinery as is exemplified in the National City (California) plant.

For manufacture of dried peel comparatively cheap machinery is needed. The peel after its separation from the fruit either by hand or machine is dried on trays in the sun. Where this is impractical a current of heated air is resorted to as a means of dehydration.

Marmalade-making machinery consists essentially of fruit slicers and cooking kettles which, from the standpoint of their capacity, are of low cost.

Equipment for the manufacture of preserved juice consists, for the most part, of ordinary bottling machinery.

In all countries the outlay for machinery is essentially the same except where oil is obtained by hand labor.

Details of factory equipment appear in the later descriptions of the different processes.

PREPARATION AND CONDITION OF THE FRUIT

Fruit for by-product manufacture must first be examined and cleaned unless it be obtained from a packing-house where cleaning has already been performed. If, on the other hand, the fruit be dirty it is best cleaned by means of brushes in the ordinary fruit-cleaning machine, together with such necessary water as the fruit may require, since adhering dirt and scale insects, while not always detrimental to the manufacture of the product, are not desirable.

The quality and quantity of the final product depends in a measure on the condition of the ripeness of the fruit especially in the manufacture of essential oils, marmalade, and juice. Thus, in the manufacture of lemon oil a green fruit gives an oil of the highest character, and fruit of whatever nature that has been subjected to a sweating process (injured by oxidation), or to slight decay or ageing, is almost unfit for the manufacture of the finer products. The quantity of oil also varies with the age of the fruit. Juice and marmalade made from oranges

early in the season have a bitter taste. Oranges from the middle of the season until its end do not give a bitter juice nor make a bitter marmalade. Not only the bitterness but the sugar content of the fruits varies. In ripe fruit the saccharine content is greatest. In lemons and no doubt in other citrus fruits the citric acid content is greatest in the unripe fruit particularly in those of summer. In the manufacture of citric acid, however, the physical condition of the fruit is not as important as in the manufacture of the essential oils.

REFERENCES FOR CHAPTER I

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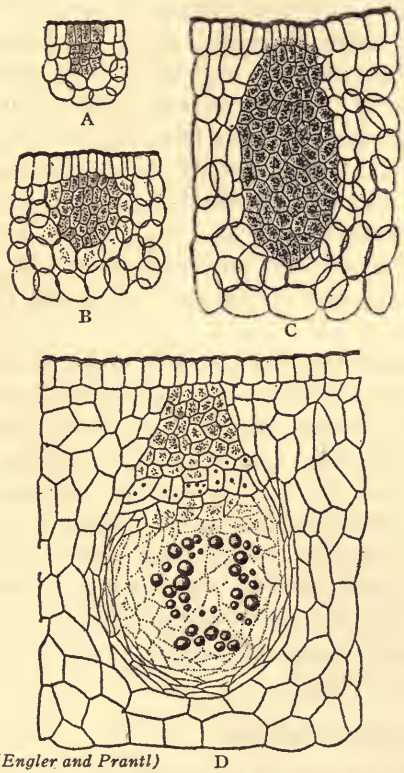
"The Use of Frozen Citrus Fruits in the Manufacture of By-Products," *California Cultivator,* LII (June 7, 1919), 773, 779.
2. FAWCETT, H. S.
"A Spotting of Citrus Fruits Due to the Action of Oil Liberated from the Rind," *Agricultural Experiment Station Bulletin No. 266* (1916). Berkeley, California.
3. WEBBER, H. J., *et al.*
"A Study of the Effects of Freezes on Citrus in California," *Agricultural Experiment Station Bulletin No. 304* (1919). Berkeley, California.

CHAPTER II

PRODUCTS FROM THE RIND—ESSENTIAL OILS

THE OIL CELLS

Even in the seedling stage, the stem of the citrus plant and its first leaves are studded with essential oil glands. If a leaf of any citrus plant is held up against the light and examined with a lens, *three* sizes of cells are quite distinct. These are the essential oil cells or glands. It should be noted that the larger ones are at certain distances from each other, and that the intermediate spaces are filled with smaller and smaller oil cells. Every citrus leaf has this peculiarity repeated in the *edge* of the leaves, the large oil cells occupying the angles between the large crenations, the smaller ones, those between the small crenations. It is curious to note that in the rind of many citrus fruits a similar disposition of large and small oil cells is maintained.



(Engler and Prantl)

FIG. 5.—Formation of oil cells in the rind of the sour orange (*Citrus Aurantium* L.) *A*, *B*, first stage; *C*, before breaking down of cell wall; *D*, after breaking down of cell wall.

The outer, or rind, surface of a citrus fruit often resembles that of a lump of dough, studded with large and small *pinhole-like* depressions, the botanical term for which is "foveoli." It is interesting to note that in cases of large fruit, where the oil cells have plenty of room to develop, the three sizes are distinct, the larger depressions corresponding to the larger oil cells, the smaller depressions corresponding to the cells of the second magnitude; those of the third magnitude are represented by still smaller depressions. In short, a longitudinal section of any part of the rind would very closely resemble, in many cases, the edge of the leaf of the malta lemon, with the difference that in the rind

section the oil cells are much more developed. In small specimens, the third-size cells are mere points.

The oil cells of the rind are usually balloon-shaped; some are pointed like the spindle-shaped cells of the pulp.

In opposition to Risso's theory, the external appearance of the oil cells of the rind has no definite relation to the *quality* of the juice of the pulp, as may be seen from the following instances: (1) two varieties of lemon, one sweet, one sour, may be superficially indistinguishable, e.g., *the nimboo* (sweet lemon) of Furruckabod and the *Kalair kaghzi* of Lucknow; (2) in one stage of the sweet orange, the *simtare* of India, the juice is sour, later the juice is a mixture of acid and sweet, while, when completely ripe, it has little acid, yet at all stages the larger oil cells have their openings concave, and the smaller ones are represented by minute *convexities;* (3) the *sadaphal,* which has scarcely a trace of acid from beginning to end, has also the two sets of oil cells on its surface; (4) finally, the *Kuthairee nimboo* has its large oil cells, which are the only ones visible on its lumpy projections, *convex,* while its juice is distinctly sour.

It would, therefore, appear that Risso's notion about the constant relationships of the concave or convex cells of the rind to the acid or sweet juice of the pulp is untenable.

According to J. von Sachs, citrus ethereal oil glands originate from a single mother-cell, which undergoes many divisions in all directions, so that a multicellular mass of tissue of roundish form arises, the cells of which subsequently become remarkable as containing very granular, apparently dead, protoplasm. Later on, the thin cell walls dissolve, the process commencing in the middle of the spheroidal group and proceeding outward. There thus arises a roundish cavity filled partly with watery sap, partly with drops of ethereal oil—the products of solution of the mass of cells. The layers of tissue surrounding this cavity fit closely on all sides, without intercellular spaces, and thus virtually form a wall or receptacle for the secretion (Bonavia).

METHODS OF OBTAINING THE OIL

The methods of securing[1] the oil from the plant may be divided into four principal classes:

[1]United States patents involving extraction of oils are: W. A. Allport and T. J. W. C. Davenport, No. 1002020, August 29, 1911 (machine for extracting oil); S. L. Ames, No. 1097607, May 26, 1914 (flavoring emulsion); A. W. Giampietro, No. 1116880, November 10, 1914 (machine); E. J. Sheehan and W. S. McKay, January 9, 1917 (process for extraction by solvents); F. A. McDermott, No. 1353169, September 21, 1920 (process); S. C. Hood, No. 1186317 (machine for peeling).

1. Distillation under normal or reduced pressure
   a) Normal
   b) Steam
2. Mechanical processes
   a) Expression by hand
   b) Expression by machine
3. Displacement
4. Extraction by solvents
   a) Volatile solvents
   b) Non-volatile oils or fats

DISTILLATION

All the essential oils are readily volatile in water vapor. Distilled citrus oils are a commercial commodity but they are of far less value than expressed oil. Citrus oils even when distilled under diminished pressure and at a low temperature (which tend to reduce decomposition) decompose more or less rapidly. Ordinary distillation of the peel leads to a decomposition of the peel with no yield of oil. Finely ground peel gives no better results. Dry steam distillation results in no yield of oil, presumably also from the decomposition of the oil. Wet steam distillation gives the best results. The pulp, when finely ground in water, is considered as in the best condition for this variety of distillation. A good yield of clear, colorless oil is obtained.

In connection with steam distillation, it is interesting to note possible catalytic action. If the distilling vessel is made of galvanized iron, i.e., lined with zinc, no yield whatever of oil is obtained. The stills employed are therefore lined with tin, silver, or glass which have no detrimental effects.

One firm produces lemon oil commercially in southern California. Distilled oil made by this firm sells at from 40 to 60 cents per pound, and is used by large soap manufacturers for scenting toilet soaps; ten pounds are obtained per ton of fruit. This oil, however, does not have the full rich odor of pressed lemon oil and is not suitable for flavoring purposes. A better grade of oil is made in the same factory by a secret process, the "cold method."

MECHANICAL PRODUCTION

a) *Expression by hand.*—The *sponge process,* which is usually employed in Sicily and Calabria is essentially as follows: The fruit is first soaked in water for a short time and the peel is then removed in three parts, each third being pressed flat by the fingers against a sponge held in the other hand. The oil glands are burst by the pressure and the oil, together with a considerable quantity of water and some juice, is absorbed by the sponge The sponge is squeezed from time to time

into a bowl and the oil thus obtained is finally separated from the water and filtered in closed filters. The oil secured in this manner is the best commercial oil of today; it has the best keeping qualities as well as the best flavor and aroma; and it forms the pharmacopœia standard. The sponge process which involves hand labor is impracticable in the United States, because of the high cost of labor. Pitino Brothers, of Los Angeles, have put this method to a thorough test with laborers formerly employed in Sicily.

The *écuelle process* is employed in Northern Italy and the south of France. An écuelle is a saucer-shaped vessel, 8–10 inches in diameter, made of tinned copper, the inside of which is covered by short spikes about a quarter of an inch long. The bottom is connected by a hollow tube through which the oil passes to a collecting vessel. The whole fruit is placed on the écuelle and by rapid rotatory motion the oil glands are burst and the oil is ejected.

In the *Scorzetta process* the fruits are cut into halves, the pulp is removed by a spoon and the peel is twisted and pressed against a sponge. The pulp is used for the production of lemon juice and the peel is salted.

Other devices involving hand labor are also used for the production of these oils. In one of them the fruits are brought into contact with small knives which puncture or rupture the oil glands. The oil may be drawn out of the vessel by means of vacuum pumps, and steam may even be admitted to facilitate the process.

b) *Expression by machine.*—Fresh unpressed peel will absorb 10 per cent of its weight of oil. By pressure applied to the macerated peel nearly all the original oil can be recovered as an emulsion. This emulsion can be decomposed by heating to a temperature of not more than 90°C. One-tenth of its volume of hot 2 per cent gelatin is then added, thoroughly mixed, and one-fourth its volume of a hot 10 per cent tannin solution is stirred in. The emulsifying agent is thus coagulated and the oil released.

In 1916 Hood invented a machine for peeling citrus fruits. This machine simply grates the rind from the fruit. It is not very successful in peeling oranges that depart from a spherical shape, as the machine then tends to peel the central portion only and not the ends of the fruits.

Experiments conducted on a laboratory scale indicate that finely ground peel subjected to centrifugal action will yield about 5 lbs. of oil per ton of fruit.

EXTRACTION BY DISPLACEMENT

A novel and mystifying method for the manufacture of lemon oil has been announced by Liotta. The lemons are pounded in a large vessel and mixed with a liquid, the composition of which is kept secret. This liquid, said to be an acid, causes the separation of the oil, which rises to the surface and is removed. A "substance" is then added which liberates the "acid," so that it can be used again while the residue, consisting of lemon juice, pulp, peels, etc., may be sold to manufacturers of citrate of lime.

It is claimed for this new method that the yield of oil is 2½ per cent higher than with the old method of pressing by hand. As regards cost, this is stated to be but 2.3 cents per 1,000 lemons, the operation requiring only twenty-two minutes. It is expected that by perfecting the method and working on a large scale, the operation can be carried out much more rapidly.

As long as no further particulars are known about the "acid" and the "substance" or the manner of recovering it, the possible usefulness of this method cannot be determined.

EXTRACTION BY SOLVENTS

So far, no essential oil of the citrus fruit is produced commercially by the volatile solvent processes.

Experiments indicate that when absolute alcohol is used as a solvent, the proteins, etc., of the rind are coagulated in such a manner as to prevent the solution of the oil. Fifty per cent alcohol on the other hand dissolves the oil readily, but also dissolves coloring matter.

Petroleum ether of 86° Baumé gives a good yield of colorless oil. However, it has been found impossible subsequently to separate all the petroleum ether from the oil; there always remains enough of the solvent to impair the odor of the citrus oil.

Ethyl ether gives similar results to those of petroleum ether. Inflammability and expense also tend to prohibit the use of this solvent.

The lemon oil produced by the volatile solvent process has much the same characteristics as that of the orange, with the exception that the oil produced from green fruit has a higher citral content than that produced from fruit which has been subjected to the sweating process, or is fully ripe.

Sheehan in 1917 patented a process for extracting essential oils by a volatile solvent. The solvent is said to be obtained from the fruit itself; its nature he does not reveal although he says it may be obtained also from other sources.

The extraction by non-volatile solvents is typified by the enfleurage process, used to obtain the perfumed oil from the flowers. A pure neutral fat, such as purified lard, is melted and poured onto trays, technically known as "chassis" and the flowers are laid on the fat for

a short time, then removed and replaced by fresh flowers until the fat has become saturated. The treated fat is sold as "pomades," or is employed in the manufacture of perfumes, being extracted by means of warm alcohol in closed vessels. Such extractions are not at present commercial in the United States (see chapter viii).

FRUITS YIELDING OIL

Oil may be obtained from the rind of all citrus fruits. Commercially the lemon yields the most important oil manufactured in largest quantities. The bergamot, the citron, the grape fruit, the limes, the mandarin, the bitter and the sweet orange, all furnish valuable essential oils.

OIL OF BERGAMOT

Origin and production.—The bergamot tree (*C. Bergamia* Risso) is cultivated exclusively in Calabria, the pear-shaped, pale yellow, thin-skinned fruit being used for oil production only. In Sicily the tree does not thrive.

Properties.—Oil of bergamot is a brownish-yellow or honey-colored liquid often colored green by the presence of copper or chlorophyll (Liotta, 1899). It has a bitter taste and a very pleasant odor. Its specific gravity at 15° is 0.881–0.886. The angle of rotation, which on account of the dark color of the oil can mostly be determined only in a 50 or 20 mm. tube, varies from +8° to +22°. However, optical rotations as low as +5°24′ and as high as +24° have been observed;[1] $n_{D20°}$ 1.464 to 1.468; acid value 1 to 3.5.[2]

The oil yields a clear solution with about one-quarter to one-half volume of 90 per cent alcohol, and the solution does not become turbid on the addition of more alcohol. All oils do not dissolve clearly in 80 per cent alcohol. Many, and especially those of a high ester content, often give turbid mixtures, from which fatty globules separate on the bottom on standing. The reason for this phenomenon has not yet been determined, but can probably be sought in the waxlike constituents which get into the oil during expression. This non-volatile substance, which partly separates as a deposit when the oil is kept for some time, consists principally of bergaptene. It remains in the residue when the oil is evaporated on a water bath or by rectification; it amounts to 5–6 per cent.

Rectified oil of bergamot is colorless and has a lower specific gravity (0.65–0.875) as well as a slightly higher rotatory power than the orig-

[1] *Report of Schimmel & Co.* (April, 1910), p. 59.
[2] *Ibid.* (April, 1908), p. 40.

inal oil. The rectified oil is as a rule less valuable because during the steam distillation part of the ester is always decomposed.

The amount of ester present is a measure of the value of bergamot oil, i.e., the oil is the better the more linalyl acetate it contains. Although the average content of ester varies somewhat in different years, it usually amounts to between 34 and 40 per cent, but sometimes rises as high as 45 per cent. Even within the limits of the same harvesting period great variations occur. The oils obtained at the beginning of the harvest from less ripe fruit contain less (down to 30 per cent linalyl acetate); with increasing ripeness the ester content increases, for which reason the oil expressed from ripe fruit is the best.

Composition.—As early as 1840 Soubeiran and Capitaine called attention to the presence of different terpenes in bergamot oil. Wallach showed in 1884 that *d*-limonene was contained in the fraction boiling from 175°–180°. When he heated the fraction of the oil boiling from 180°–190°, which, indeed, absorbed bromine but yielded no solid bromide, to a higher temperature, high-boiling condensation products were formed, and on again fractionating, the portion going over up to 190° gave dipentene tetrabromide melting at 124°–125°. It does not follow from this, whether the dipentene detected in this manner is to be considered as an original constituent of the oil, or whether it has been produced by heating the fraction 180°–190° which no doubt contained linalool. Likewise, the observation made by Semmler and Tiemann in 1892, according to which the oil boiling 17° higher than the limonene fraction yielded dipentene tetrabromide, cannot be considered as a proof of the presence of dipentene in bergamot oil.

Our knowledge of the most important constituent as far as the odor of the bergamot oil is concerned is due to two investigations, published at nearly the same time, by Semmler and Tiemann, and by Bertram and Walbaum. By these investigations it was shown that the principal carrier of the bergamot odor is the acetic ester of *l*-linalool.

In addition to this ester, free *l*-linalool and possibly substances not yet isolated take part in the formation of the aroma.

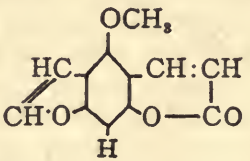
According to F. Elze, three other alcohols are contained in bergamot oil. He examined a fraction which, on a factory scale, was obtained to the extent of 25 per cent in the production of terpene-free bergamot oil. After saponification, distillation with water vapor, and fractionation, it yielded an oil with the following properties: $d_{15°}$ 0.890; α_D −10° (in a 100-mm. tube). Treated with phthalic acid anhydride, a small amount of an oil was obtained which proved to be dihydrocuminic alcohol (melting-point of naphthyl urethane 146° to

147°) and which upon oxidation with Beckmann's chromic acid mixture yielded an aldehyde boiling at 235° and had a cumin-like odor. Regenerated from its semicarbazone (melting-point 198° to 199°) $d_{15°}$ was 0.970 and α_D —39°. The bulk of the alcohol mixture, however, consisted of nerol ($d_{15°}$0.880) which was further characterized by its tetrabromide, melting at 118°, and its diphenyl urethane, melting at 50°.

In that portion which did not react with phthalic acid anhydride, Elze proved the presence of the terpineol melting at 30° (melting-point of the phenylurethane 110°). This observation is very important since it has been found recently that bergamot oil is occasionally adulterated with terpinyl acetate.[1] Hence it is a mooted question at present whether terpineol is a normal constituent or not.

Charabot has made a comparative study of the oils of bergamot from the green and the ripe fruit. The oil from the green fruit had a specific gravity of 0.882 at 14°, α_D is +14°38′; it contained 0.289 per cent of free acid, 33.8 per cent of linalyl acetate, 13.9 per cent of linalool, and 5.9 per cent of bergaptene. The oil from the ripe fruit had a specific gravity of 0.883; α_D is +20°30′, 0.283 per cent of acid, 37.3 per cent of ester, 5.9 per cent of linalool, and 5.5 per cent of bergaptene. He draws the conclusion that in ripening the original linalool is changed to the ester and that during this process some of the linalool is dehydrated with the formation of terpenes.

The bergaptene contained in the oil to the extent of about 5 per cent is completely odorless. A whole series of investigations has been carried out on this compound.[2] Pomeranz in 1891 succeeded in clearing up its constitution. Bergaptene, $C_{12}H_8O_4$, forms soft, white, satin-like, tasteless needles, which are odorless at ordinary temperatures, but on heating give off aromatic vapors, and melt at 188°. Bergaptene is the monomethyl ether of a dioxycumarin which is traceable to phloroglucin. By treating with methyl iodide and alcoholic potassium hydroxide methyl bergaptenic acid and its methyl ester result. According to this, bergaptene is the inner anhydride of bergaptenic acid. H. Thoms and E. Baetcke assign to it the following formula:



It is isomeric with xanthotoxin.

[1] *Report of Schimmel & Co.* (April, 1910), p. 60.

[2] See Mulder, Ohme, Franke, Godeffroy, Tilden and Beck, Crismer, in References at end of this chapter, p. 67.

Several other constituents have been found in a bergamot oil by Burgess and Page. Although these investigators contend that the oil examined by them was pure, this does not follow from the constants recorded (viz., $d_{15°}$ 0.885; $[\alpha]_D$ +8°; ester content not mentioned). Hence the examination must be repeated with material of unquestioned purity, before octylene, pinene, camphene, and bisabolene can be regarded as constituents of bergamot oil. In the lowest fractions acetic acid (analysis of barium salt) was found. It was scarcely necessary to prove the presence of free acetic acid, since it is a well-known fact that the acids, which in the volatile oils are combined with alcohols, also occur in the free state to a slight extent. Moreover, Burgess and Page did not prove the presence of free acetic acid in bergamot oil, for they accumulated it by means of fractionation of the oil, a process by which the acid is formed from the linalyl acetate, as they themselves surmise.

Fraction 150° to 155° revealed a very low specific gravity and a low refractive index. Hence they infer the presence of an olefinic hydrocarbon, octylene. This inference Burgess and Page endeavor to substantiate by pointing out that the odor of this fraction reminds of the octylene found by the same authors in lemon oil, also by demonstrating that upon oxidation with potassium permanganate butyric acid (identified only by its odor) results.

Laevogyrate ($[\alpha]_D$ −8.3°) *α*-pinene and laevogyrate ($[\alpha]_D$ −22.8°) camphene were identified in fractions 157° to 158° and 164° to 165° respectively. The former was characterized by its hydrochloride (melting-point 125°), the latter by its conversion into *iso*borneol (melting-point 203°). The higher boiling fraction of the bergamot oil contained bisabolene (limene) $C_{15}H_{24}$ (melting-point of hydrochloride 79°).

Examinations.—Formerly the determination of the purity of bergamot oil was not difficult because adulterations then used changed the physical constants to a considerable extent. As the specific gravity of pure oils varies within the comparatively narrow limits of 0.881–0.886, the addition of turpentine oil,[1] lemon oil, orange oil, as well as distilled bergamot oil produce a decrease, fatty oil, cedar wood oil, or gurjun balsam oil an increase, in the density. A part of these adulterants would also change the angle of rotation which lies between +8° and +20° with pure oils.

Nevertheless, in spite of the normal rotation, an oil might be adulterated provided the normal limits were not interfered with by the proper selection of adulterants such as turpentine oil with lemon oil or orange oil. In order to detect such adulteration Romeo and Moricca fractionate 30 c.cm. of bergamot oil into fractions of 5 c.cm. and determine the angle of rotation of the first two fractions. In the case of pure oils, the rotation of the first fraction is greater than that of the second; in the case of adulteration, the reverse holds true.

The solubility determination with 90 per cent alcohol gives with bergamot oil results of only slight value, as by it only very extensive adultera-

[1]As bergamot oil contains no pinene, the presence of this hydrocarbon can be considered as proof of the adulteration with turpentine oil.

tions can be recognized. Only a part of pure bergamot oils, as already mentioned, is soluble in 80 per cent alcohol. If a bergamot oil dissolves to a clear solution in this solvent it is free from fatty oil, turpentine oil, and orange oil. If, however, it does not dissolve, this may be due either to an adulterant, for instance, fatty oil, or also to the presence of large quantities of bergaptene or waxlike constituents.

The detection of fatty oil is effected by weighing the residue left by evaporating the oil at 100°, which with normal oil amounts to 4.5–6 per cent.

About 5 gm. of oil (weighed accurately to .01 gm.) are weighed off in a glass or porcelain dish and heated on a water bath until that which remains has lost all odor of bergamot oil. After cooling, the dish, previously tared, is weighed with the residue. If this amounts to more than 6 per cent of the oil used, fatty oil is present. Each additional per cent represents 1 per cent of adulterant. Thus, e.g., a bergamot oil adulterated with 5 per cent of olive oil will have a residue of from 10 to 11 per cent.

In the oils adulterated with turpentine oil, orange oil, or distilled bergamot oil, the residue will in certain cases amount to considerable less than 5 or 6 per cent.

The determination of the residue is of special importance as fatty oil gives a high saponification number and may, therefore, easily give rise to mistakes.

Ester content.—The determination of the ester content[1] not only allows the detection of adulterations, but also furnishes a criterion of the quality of the oil. This is the better, the greater the amount of linalyl acetate.

By the saponification, the addition of the essence obtained by the distillation from the press residues or the small rejected fruit,[2] which shows a much smaller saponification number than the expressed oil, is also detected.[2]

How far, under certain circumstances the adulteration may be carried, is shown by two samples of "artificial bergamot oil" which were submitted to Schimmel and Co.[1] for analysis. The oils had the following constituents: (1) $d_{15°}$ 1.0432; α_D 7°30′; acid value 0.3; ester value 403.3. (2) $d_{15°}$ 1.0858; α_D +7°30′; acid value 0.9; ester value 577.1.

Even for artificial oils, density and ester values are abnormal to such an extent that from them alone the peculiar composition of the oils may be judged. Based on the ester value, the ester, calculated for linalyl acetate, would be 141 per cent and 202 per cent respectively—figures which are quite impossible and from which it can be deduced at once that considerable

[1]As according to A. Bornträger (*Zeitschrift für analytische Chemie,* XXXV [1896], 35) the evaporation residue on saponification gives numbers which correspond to an amount of 2 per cent of linalyl acetate, this number ought by right to be deducted from the result found. This is, however, not done, as the method would thereby be only made unnecessarily complex.

[2]An oil obtained in Messina by distillation from the expressed bergamot peel possessed an ester content of only 12 per cent (specific gravity 0.865). Two oils distilled from the peel of fallen unripe bergamot fruit contained 6.3 and 23.5 per cent of ester (specific gravity 0.868 and 0.889) (*Report of Schimmel & Co.* [October, 1894], p. 15).

[1]*Report of Schimmel & Co.* (October, 1914—April, 1916), pp. 18–20.

quantities of esters are present which should not be found even in artificial oils. Further examination revealed the fact that in both samples these esters were not linalyl acetate, as should be the case in artificial bergamot oil, but mostly bodies of no value for the odor, namely, phthalic acid esters in one sample (probably diethyl phthalate) and glyceryl acetate in the other. As both oils contained about 70 per cent of these bodies respectively, the proof of their presence was easy, in spite of the smallness of the samples. Glyceryl acetate was isolated by shaking out with a 5 per cent solution of alcohol and was recognized, i.e., by the high saponification value (676) whereas in the other oil the acid, which did not pass over with steam in the determination of the acid number II (*Report* [October, 1910], p. 61) was identified as phthalic acid (melting-point 203°; melting-point of the anhydride obtained by sublimation 130°; fluorescein reaction).

As mentioned above, both samples contained about 70 per cent of these esters, that is to say, such an extent that one cannot speak of artificial oils any longer, but more correctly of cheap—and from the point of view of their strength—valueless esters which had been perfumed more or less cleverly so as to resemble bergamot oil. Such adulterated substitutes have, needless to say, nothing in common with a scientifically prepared artificial bergamot oil.

It is easily explicable why during the Great War many volatile oils which only occurred rarely in trade or were almost wholly exhausted should have been subject to adulteration. Bergamot oil belongs to this class; the few samples which were submitted for inspection[1] were nearly all adulterated.

A sample from Messina which had been sent them from Switzerland showed the following characteristics: $d_{15°}$ 0.8761; α_D +28°; acid value 2.7; ester value 70.0 equals 24.5 per cent ester, calculated as linalyl acetate. The constants prove quite alone that the oil was an inferior, adulterated product. The specific gravity is too low, the degree of rotation much too high and the ester content, which in a good trade sample ought not to be under 34 per cent, quite insufficient. The high rotation indicates an admixture of lemon oil.

Two other specimens were of such quality that it was difficult to decide whether they were adulterated oils or artificial products. One of them showed the following characteristics: $d_{15°}$ 0.8866; α_D +15°; residue on evaporation 6 per cent (liquid); acid value 0.9; ester value 59.7 equals 20.9 per cent ester calculated as linalyl acetate; soluble in one volume and more of 80 per cent alcohol. In this case also the much too low ester content immediately characterized the oil as quite inferior. Strange to say, the oil, in spite of its very low ester content, dissolved surprisingly well in alcohol, as the majority of bergamot oils do not give a clear solution in 80 per cent alcohol. Even in the case of the oils that are soluble in it the diluted solution is nearly always turbid; that is all the more to be expected from an oil with a low ester content. Another anomaly finds its expression in the quality of the residue on evaporation which in this case was liquid, instead of butter-like in consistency. All these facts indicate not a natural oil at all, but an unsuccessful artificial product.

[1] *Report of Schimmel & Co.* (April–October, 1917), pp. 16–17.

The same holds good of a second sample which gave the following constants: $d_{15°}$ 0.8864; α_D +15°46′; acid value 37; ester value 110.1; saponification number 113.8; acid value II 63.5; difference between saponification value and acid value II 50.3; residue on evaporation 19.3 per cent. The quality of this product was betrayed by the too great difference between the saponification value and acid value (normally not above 10), as well as by the much too great a residue on evaporation (normally 4.5 to 6 per cent). The sample apparently consisted only of a fatty oil and probably contained none of those waxlike components which are so characteristic of bergamot oil. As fatty oils have a high saponification value, the object was apparently to suggest the presence of a bergamot oil rich in linalyl acetate, as the above-mentioned ester value would lead to the assumption of about 38.5 per cent linalyl acetate. In reality, however, this content is considerably smaller and can approximately be calculated from the acid value II, which would correspond to a linalyl acetate quantity of 22.2 per cent. As indicated above, this oil also gave the decided impression of an artificial product the manufacture of which had been a complete failure.

A sample with the proud label "Oleum Bergamotte la Reggio rect. pur.," handed by a Leipzig firm to the same chemists for investigation, was simply artificial, about 80 per cent linalyl acetate, as its constants prove: $d_{15°}$ 0.8997; α_D −10°11′; $n_{D20°}$ 1.45082; acid value 1.9; ester value 233.3, corresponding to 81.7 per cent linalyl acetate soluble in 2.7 vol. and more of 70 per cent alcohol.

Other constituents.—While washed bergamot oil shows a small saponification number, no attempt has been made to determine the esters present in it, but it might be expected from the analogy of this oil with the other citrus fruit oils that both linalyl- and geranyl-acetate are present.

From the analysis and the distillation figures it would seem that the constituents present in the oil are in about the following proportion:

	Per Cent
d-Limonene	90–92
Citral	3–5
α-Pinene	0.5–1.5
Geraniol	1.0–2.0
Linalool	1.0–2.0
Citronellal	Some
Linalyl and geranyl esters	Some

The oil has a very pleasing odor and flavor and when 30 per cent by volume of pure ethyl alcohol is added it appears to keep as well as either lemon, orange, or lime oil. Its properties seem to place it between the lemon and the orange in value.

Methods of production.—The photographs on Plates I and II illustrate the details of the operation of the extraction of oil of bergamot on the estate of M. le Commandatore Spinella at Lazarro.

Plate I shows a view of the workshop where the pressing is carried out by means of the machine shown there. This machine is composed of a wheel with pegs turning a drum with bars ending in the bowl. This bowl is a kind of plate, 20 cm. in diameter, provided with copper points

(*Roure-Bertrand fils*)

MANUFACTURE OF THE OIL OF BERGAMOT IN CALABRIA.

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1 cm. long and fitting exactly in a cylinder the bottom of which constitutes a second similar plate on which the fruits are placed. By its weight, the drum presses the fruits, the points of the two bowls tear up the rinds and the liquid which escapes flows into a receiver placed at the lower part of the machine.

Plate II shows the particular means employed for the filtration of the essential oil. The crude oil coming from the machine is placed in filters of coarse flannel which are tied at the top in such a way as to form a sort of pocket. These are then suspended from iron rods, after having been cased with a metal arrangement as shown in the figure. The conical portion of this receiver, loaded with weights, presses the bulging sides of the filter, which assists and hastens the flow of the liquid into the lower portion of the receiver, from which it is withdrawn by the tap. There is thus obtained a mixture of essential oil and water which is subjected to decantation.

Each apparatus is tended by three men, one to turn the crank, one to sort the fruits, selecting those of an equal size in order that the pressure may be exerted uniformly, and one to clean out the bowl when the fruits have been pressed.

The fruits from which the essential oil has been pressed are next subjected to the action of large presses; the juice obtained is utilized for the manufacture of calcium citrate.

The method for controlling the exhaustion of the rinds of the fruits is a most simple one and is worth describing. The foreman of the factory peels a fruit which has come out of the bowl. He then presses the peel between his fingers holding it a short distance from the flame of a lamp which is held by an apprentice. If the pressing has been badly done, fine droplets of essential oil are projected out, making so many small brilliant flames, which indicate bad workmanship.

This work is done at night time, in order to avoid too great evaporation. The essential oil produced by the machine is far superior to that yielded by the method called "by the sponge." The latter, in fact, is no longer used for the bergamot, except in the case of fruits which are too small to be treated in the machine.

In Calabria lemons are also expressed with the aid of this machine. However, the oil thus obtained is invariably green (see Properties on p. 24) and is not salable as such, but is said to be used for the adulteration of bergamot oil.

OIL OF LEMON

This oil is obtained by expression of the fresh peel of lemons (*Citrus limonia* Osbeck) and is produced chiefly in Sicily and on the Riviera. Chemically, it is probably one of the most complex of the essential oils.

Properties.—Lemon oil is a light-yellow liquid possessing the agreeable odor of fresh lemons and an aromatic, mild, and, somewhat later, bitter taste. Inasmuch as oils produced in geographically contiguous districts reveal decided differences in their properties, it is difficult to

establish limit values of general applicability. Moreover, the season and degree of maturity of the fruit exert a marked influence on the properties of the oils. Thus, e.g., the oils expressed from the fruits collected in November reveal the highest optical rotation, but this diminishes with the increasing maturity of the fruit as the winter advances. At the same time specific gravity and citral content increase. A shortage of oil sometimes occurs when a crop of fruit is small, and lemons are then expressed which in normal years would be used for other purposes. This happened in 1913, when the price of lemon oil rose to the height of $10.23 per 1 kg. During the months of April and May of that year much oil was expressed from the so-called bianchetti lemons, which revealed a low citral content and an angle of rotation as low as +54°. It is further noteworthy that climatic conditions, such as continued drought or cold weather, influence the properties of the oil.

Generally the *specific gravity* lies between 0.856 and 0.861, but 0.854 has been observed as a lower limit in connection with pure oils.

The *optical rotation,*[1] as a rule, fluctuates between +57° and +61°. However, certain districts, more particularly in the western part of the island, produce oils with an angle of rotation of but +56°. In one instance Chace observed this to be as low as 54.16°. In other districts the angle of rotation rises to +67°.

The *evaporation residue,* the determination of which is discussed under bergamot oil, varies between 2.1 and 4 per cent. However, in oils obtained by the machine process it is higher and rises to 5 (Berté and Romeo) and even 6.6 per cent. Acid value of the evaporation residue 19 to 39; ester value 100 to 214. However, the ester value of small amounts of evaporated oil (5 to 10 gm.) does not drop below 150, whereas that of the residue of larger amounts of oil has been observed as low as 100. This apparently is due to the resinification because of the longer period of evaporation.

The *index of refraction* $n_{D20°}$ lies between 1.474 and 1.476.

Solubility: because of the mucilaginous and waxlike substances which accompany the citrapene (see under Composition, p. 28) the oil is mostly not perfectly soluble in (6 to 8 volumes of) 90 per cent alcohol. However, it forms a clear solution with 0.5 to 1 volume of 95 per cent alcohol and with every proportion of absolute alcohol, ether, chloroform, benzene, and amyl alcohol. Because of the slight water

[1]It is necessary to determine the angle of rotation at 20° or to compute it with reference to this temperature. If the determination is made at a temperature below 20°, 9 minutes should be deducted for every degree below 20°; if made above 20°, 8.2 minutes should be added for every degree in temperature.

content of the oil, its solutions in carbon disulphide and benzin are mostly turbid.

The citral content of lemon oil varies from 3.5 to 4 and even 5 per cent when determined according to Kleber's method. (For details see p. 64 under Examination.)

As to the optical rotation of the first 10 per cent of fractionated distillate, see p. 29.

Effects of storage.—Like all volatile oils obtained by expression, lemon oil deposits a more or less crystalline sediment upon standing.

Both air and light cause rapid changes: the oil loses its color and a viscous, brown mass is deposited. At the same time the specific gravity as well as the solubility in 90 per cent alcohol is increased. These changes correspond to those observed in connection with old turpentine oil that has been stored improperly. Hence, lemon oil should be kept in well-filled, closely stoppered containers, stored away from light and in a cool place.

PROPERTIES OF TERPENE-FREE LEMON OIL

As pointed out on page 66 the methods by which the terpene-free lemon oils (Boecker) are prepared by the several manufacturers differ greatly, hence the products differ accordingly. It is, therefore, impossible to establish limit values. Moreover, a distinction is made between those deprived merely of their terpenes and those deprived of both terpenes and sesquiterpenes.

In connection with a number of such concentrated oils, Parry (1913) has observed the limit values given in Table I.

TABLE I

	Terpene-Free	Free of Terpenes and Sesquiterpenes
$d_{15°}$	0.8935 to 0.899	0.898 to 0.902
α_D	−5° to −8°30′	1° to −3°45′
n_D	abt. 1.4810	.....
Citral	42 to 48 per cent	An average of 65 per cent or somewhat higher

In connection with two terpene- and sesquiterpene-free oils made by himself, Boecker observed the following constants: $d_{15°}$ 0.8951 and 0.8971; −7°10′ and −5°40′; the one oil required 1.4 volume of 80 per cent alcohol to form a clear solution, the other 0.9 volume.

For the determination of the hydrocarbon and citral contents of concentrated oils see page 33.

PROPERTIES OF OTHER SPECIAL OILS

An authentic sample of oil prepared by the machine process had the following properties: color green; $d_{15°}$ 0.8630; $a_{D20°}$ +58°5′; of the first 10 per cent $a_{D20°}$ +56°34′; $n_{D20°}$ 1.47695; evaporation residue 6.6 per cent with an acid value of 25.5 and an ester value of 136.7; citral content 6 per cent.[1]

The constants of a Spanish lemon oil were as follows: $d_{15°}$ 0.862; $a_{D20°}$ +63°32′; $a_{D20°}$ of the first 10 per cent +67°10′.

In connection with a California oil[2] the following constants were found: $d_{15°}$ 0.8598; $a_{D20°}$ +53°56′; a_D of the first 10 per cent +48°42′; $n_{D20°}$ 1.47490; evaporation residue 3.6 per cent.

The color of a concrete oleoresin of lemon was dark olive; $d_{15°}$ 0.8730 to 0.8836; $a_{D20°}$ +57°30′ to +60°30′; a_D of the first 10 per cent +54°11′ to +69°40′; evaporation residue 14.2 to 15.4 per cent; acid value of the evaporation residue 25.4; ester value 102.1; citral content 6 per cent.

Properties of lemon oil terpenes: $d_{15°}$ 0.852 to 0.854; $a_{D20°}$ +62° to +72°; $n_{D20°}$ 1.473 to 1.475; soluble in 6 to 7 volumes or more of 90 per cent alcohol and in 1.7 volumes or more of 95 per cent alcohol.

Composition.—Although lemon oil has long been known, it required a relatively long time to acquire an even superficial insight into this complex mixture. The study of its numerous components was not rendered more easy by the presence of non-volatile constituents since their removal, even by steam distillation, could not be effected without practical decomposition of the volatile constituents.

A critical study of the extensive literature,[3] which cannot be taken up in detail, reveals the fact that some of the oils examined formerly were adulterated with turpentine oil. This is not surprising for it has only recently been demonstrated that lemon oil should contain, at most, traces of pinene.

The early analyses of the oil revealed its low oxygen content. Individual chemists even went so far to declare it to be free from oxygen. This error resulted from the practice of using rectified oils for investigation, in the preparation of which the oxygenated constituents remained in the residue.

Arranged according to their boiling-points, the following constituents have thus far been observed: (1) octylene, (2) α-pinene, (3) camphene, (4) β-pinene, (5) β-phellandrene, (6) methylheptenone, (7) γ-terpinene, (8) *d*-limonene, (9) octylic and nonylic aldehydes, (10) citronellal, (11) α-terpineol, (12) citral, (13) linalyl acetate,

[1] Unless otherwise stated the citral content is determined by the Kleber method.
[2] *Report of Schimmel & Co.* (October, 1905), p. 28.
[3] See under Saussure, Dumas, Blanchet and Sell, Soubeiran and Capitaine, Gerhardt, Berthelot, Oppenheim, Lafont, in the References at end of the chapter, page 67.

(14) geranyl acetate, (15) bisabolene, (16) cadinene, (17) acids, (18) citroptene, citraptene, or lemon camphor.

1. Octylene (?). In connection with the study of the more volatile constituents of large quantities of lemon oil, Burgess and Page (1904) isolated a hydrocarbon possessing the following properties: d 0.7275; $\alpha_D \pm 0°$; $n_{D15°}$ 1.4066; boiling-point 123° to 124° (768 mm.); molecular refraction 38.54. Molecular weight determination and elementary analysis yielded values corresponding with the formula C_8H_{18} or C_8H_{16}. Inasmuch as the hydrocarbon yielded butyric acid upon oxidation with potassium permanganate, Burgess and Page concluded that it is octylene and regard it as a normal constituent of the oil.

2. α-Pinene. At times this terpene seems to be wanting entirely, at times it is present in such small amounts that its detection is coupled with difficulty. On account of the importance as to whether pinene is a natural constituent of lemon oil, Schimmel[1] in 1897 endeavored to isolate the hydrocarbon by careful fractionation of 50 kg. of lemon oil in vacuum. However, they obtained but 0.016 per cent distilling below 170°. Inasmuch as this fraction did not possess the properties of pinene and since a second experiment yielded like results, the chemists of this firm denied its presence. From a corresponding laevogyrate fraction Burgess and Child (1901) later obtained a hydrochloride addition product that melted at 124°, hence concluded the presence of *l*-pinene. A further investigation of the subject[2] led to the identification of a very insignificant amount of pinene by means of its nitrol benzylamide. Still later Schimmel[3] examined thirty-six samples of lemon oil obtained from reliable sources and found traces of pinene in each.

From these investigations the conclusion may be drawn that pinene frequently occurs in minimal amounts in normal lemon oil, but that occasionally it is completely wanting. Under what conditions the lemon tree produces pinene and under what conditions it produces oil free from pinene, has not been ascertained.

A method worked out by Chace for the detection of minimal amounts of pinene in lemon oil is described in detail on page 30.

3. Camphene. Schimmel[4] having expressed the opinion that camphene might be contained in lemon oil, its presence was demonstrated by Burgess and Child (1903) by the preparation of *iso*-borneol from the corresponding fraction.

4. β-Pinene. From fraction 165° to 168° Gildemeister and Müller[5] obtained, upon oxidation, nopinic acid (melting-point 126°) and nopinone (melting-point of semicarbazone 188°) thus proving the presence of β-pinene in the oil.

[1] *Report of Schimmel & Co.* (April, 1897), p. 19; (October, 1897), p. 22.
[2] *Ibid.* (April, 1902), p. 32; (October, 1902), p. 38.
[3] *Ibid.* (October, 1908), p. 50.
[4] *Ibid.* (October, 1902), p. 39.
[5] *Wallach-Festschrift,* p. 441. Göttingen, 1909; also *Report of Schimmel & Co.* (October, 1909), p. 63.

5. β-Phellandrene. This was first detected by Schimmel[1] and identified by its nitrite melting at 102°. This was verified by Gildemeister and Müller[2] who, upon oxidation with dilute permanganate solution, obtained a liquid glycol which, when boiled with dilute hydrochloric acid, yielded a hydrocuminic aldehyde the semicarbazone of which melted at 203° to 204°.

6. Methylheptenone. If the mixture of aldehydes and ketones, separated from the oil by means of bisulphite, be fractionated, methyl heptenone can be identified in fraction 174° to 179° by means of elementary analysis and the semicarbazone melting at 136° to 137°.[3]

7. γ-Terpinene. Upon oxidation of the hydrocarbon boiling above 173°, Gildemeister and Müller[4] obtained the erythritol of γ-terpinene (melting-point 237°), thereby proving for the first time the presence of this terpene in a volatile oil.

8. *d*-Limonene. This is quantitatively the principal constituent of the oil (melting-point of tetrabromide 104° to 105°).[5]

Tilden pointed out that the limonene from lemon oil is much less pure than that obtained from oil of orange. Upon oxidation of the limonene fraction, designated by him as citrene, he obtained paratoluic acid and terephthalic acid, two acids which do not result upon the oxidation of the corresponding fraction of orange oil. Citrene also behaves differently from limonene when treated with concentrated sulphuric acid. As with limonene, resinification, due to the formation of polymeric products, results. In addition, however, cymene, $C_{10}H_{14}$, can be identified among the products readily volatile with water vapor. Naturally the presence of cymene after the application of so energetic a reagent as sulphuric acid cannot be regarded as proof of its presence in the original oil. It is more likely that the cymene resulted from the phellandrene or from the γ-terpinene discovered much later. As a matter of fact neither cymine nor pseudocumene[6] have thus far been found in lemon oil not previously treated with sulphuric acid.[7]

9. Octylic and nonylic aldehydes. According to Burgess (1901) lemon oil contains an aldehyde with a cocoanut-like odor that boils between 80° and 85° (15 mm.). Von Soden and Rojahn have shown that there are, in reality, two aldehydes. Judging from the semi-carbazones obtained, they are of the opinion that the mixture consists of much nonylic aldehyde with little octylic aldehyde.

10. Citronellal was found by Doebner in oil of lemon. When condensed with pyruvic acid and β-naphthylamine, citronellal-β-naphthocin-

[1] *Report of Schimmel & Co.* (October, 1897), p. 26.

[2] *Op. cit.*, p. 441.

[3] *Report of Schimmel & Co.* (October, 1902), p. 39.

[4] *Op. cit.*, p. 443.

[5] Wallach, *Liebigs Annalen der Chemie*, CCXXVII (1885), 290.

[6] After treating citrene with sulphuric acid, G. Bouchardat and J. Lafont (*Journal de pharmacie et de chemie*, Vol. XXVII, Series 5 [1893], p. 49) found both cymene and pseudocymene in the reaction product. They seemed to regard both as pre-existing in the oil of lemon.

[7] *Report of Schimmel & Co.* (October, 1897), p. 26. Gildemeister and Müller, *op. cit.*, p. 451.

choninic acid, melting-point 225°, results. Its presence in lemon oil being thus established, von Soden and Rojahn later verified this by the preparation of the semicarbazone (melting-point 83° to 84°) from the aldehyde fraction boiling in the neighborhood of 200°.

Apparently the earlier statement of Ladell, who examined a terpene-free lemon oil, pertains to citronellal. By means of fractionation he isolated a dextrogyrate substance boiling at 206° and having the composition $C_{10}H_{18}O$.

As a constituent of lemon oil, Tilden describes a substance that boils slightly above 200° and has the formula $C_{10}H_{18}O$. With the exception of the optical rotation its principal properties corresponded with those of terpineol. Like Ladell, Tilden probably worked with a mixture of terpineol and citronellal. Barbier and Bouveault, also Burgess and Child (1902) deny the occurrence of citronellal in oil of lemon.

11. *α*-terpineol has been found in the higher boiling fractions which had been freed from aldehydes. It was identified by means of its phenyl-urethane melting at 110°.[1]

12. Citral. From the aroma point of view, citral, $C_{10}H_{16}O$, is the principal constituent of the oil. This aldehyde was discovered in 1888 by Bertram in oil of lemon.[2] The amount of this aldehyde varies between 3.5 and 5 per cent (Kleber's method). For its assay see pages 57–65.

13 and 14. Linalyl and geranyl acetates. According to Umney and Swinton the lemon oils of Messina and Palermo contain geranyl acetate. From so-called concentrated oils, i.e., from the high-boiling fractions rich in oxygen, they removed the aldehydes with hot bisulphite solution and saponified the non-aldehyde constituents. From the alkaline solution they separated acetic acid, and from the oil a fraction which formed a solid derivative with calcium chloride and which upon oxidation yielded citral. Hence they regard it as geraniol, which occurs in the original oil as acetate. From Palermo lemon oil they isolated, in addition to geraniol, a fraction having the properties of *l*-linalool. Umney and Swinton are of the opinion that the differences in the odor of the lemon oils from Palermo and Messina are due not only to the differences in the ratio between citral and citronellal of the two oils, but also to the presence of linalyl acetate in the Palermo oil.

15. Bisabolene. The occurrence of a sesquiterpene in lemon oil was first pointed out by Oliveri. Schimmel[3] determined the constants of this hydrocarbon and pointed out its remarkably low specific gravity. Burgess and Page obtained a hydrochloride melting at 79° to 80° and established its identity with the limene previously obtained by them from oil of limes. The identity of both sesquiterpenes with the known bisabolene, previously isolated from Bisabol myrrh (Tucholka) was established by Gildemeister and Müller.[4]

16. Cadinene. Bisabolene is accompanied by a higher boiling sesquiterpene which likewise yields a hydrochloride. On account of the small

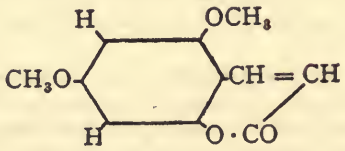
[1] *Report of Schimmel & Co.* (October, 1902), p. 40.
[2] *Ibid.* (October, 1888), p. 17.
[3] *Report of Schimmel & Co.* (October, 1903), p. 26.
[4] *Op. cit.*, p. 448, and *Report of Schimmel & Co.* (October, 1909), p. 64.

amount available, its melting-point could by recrystallization not be brought higher than 110° to 113°, but all of its properties suggested cadinene.

17. Acids. According to von Soden and Rojahn acids can be removed from lemon oil by shaking it with sodium bicarbonate solution. When the solution of sodium salts is acidulated with sulphuric acid and shaken with ether a small amount of acids is obtained, which are in part volatile, in part non-volatile. The latter shows a light-blue fluorescence and dissolves in alkali carbonates with a beautiful light-blue color.

Parry (1900) is of the opinion that traces of the methyl ester of anthranilic acid are present in the oil.

18. Citroptene, citraptene, or lemon camphor. Upon prolonged standing the expressed lemon oil separates a waxy, soft, more or less slimy mass, which likewise remains as a yellowish-brown residue when the oil is rectified or evaporated. Concerning its composition there exists an extensive literature.[1] Schmidt, however, first succeeded in revealing the constitution of citroptene which is identical with limettin. Upon treating the distillation residues of lemon oil with ether, citroptene is obtained as granular, crystalline mass. It is insoluble in ether and after repeated crystallization from acetone and methyl alcohol, and finally from dilute alcohol to which animal charcoal has been added, it is obtained as shiny, colorless needles that melt at 146° to 147°. The solutions reveal a violet-blue fluorescence. Analysis reveals the composition $C_{11}H_{10}O_4$ and methoxyl determinations, the presence of two methoxyl groups. Fusion with potassium hydroxide yields phloroglucinol and acetic acid. In chloroform solution citroptene combines with bromine to form a dibromide $C_{11}H_{10}Br_2O_4$, that melts between 250° and 260°. The supposition that citroptene is a methylated dihydroxy cumarin was confirmed by synthesis. Starting with phloroglucinol, Schmidt converted this into phloroglucin aldehyde and from this, upon cumarin synthesis, a dihydroxy cumarin which, upon methylation, yielded a compound corresponding in its properties with citroptene. It melted at 146° to 147°. Hence citroptene is represented by the following formula.



In addition to citroptene and other compounds, Schmidt found in the lemon oil residues a phenol melting at 89° which dissolves in sulphuric acid with a deep-red color but does not react with ferric chloride.

Examination.—The examination of lemon oil as to its purity is one of the most difficult tasks of the analytical chemist. As has already been pointed out, the properties of the oils vary considerably with the districts in which they are produced, also with the periods of the year in which the fruit is harvested. To these difficulties there should be added the uncer-

[1]See under Mulder, Tilden and Beck, Crismer, Theulier, Burgess, in References at end of chapter, p. 67.

tainty to detect the addition of hydrocarbons which result upon the production of terpene-free oils, provided this addition is restricted to certain limits. A further difficulty exists in the presence of non-volatile substances which interfere with the isolation and assay of such constituents as citral. Indeed, the citral assay of lemon oil is one of the most difficult of tasks. Because of the low citral content of the oil, its assay must be extremely exact in order to utilize the results as a means of detecting the additions of non-aldehydic substances. It should further be remembered that adulterators can readily bring the citral content of an adulterated oil up to the required standard.

Gross adulterations can be detected by the determination of the specific gravity and angle of rotation. Important conclusions can also frequently be drawn from the amount of evaporation residue. Adulterations with turpentine oil can be detected in most instances by a comparison of the optical rotation of the first 10 per cent of distillate with that of the original oil. The solubility test according to G. Patanè (cf. p. 31) has not yet been corroborated sufficiently by experience to judge its value. Neither has the viscosity determination (see p. 32) found its way into practice.

THE DISTILLATION TEST

The distillation test is used principally for the detection of turpentine. In spite of the addition of turpentine oil, an adulterated oil of lemon may reveal a normal optical rotation provided the reduced rotation is compensated by the addition of orange oil. Such an adulteration may, however, be detected by the optical examination of special fractions of the oil. In the case of pure oils, the angle of rotation of the first 10 per cent of distillate is but 5° to 6° lower than that of the original oil.[1] For oils to which turpentine oil has been added the difference is greater. For this distillation test a Ladenburg fractionating flask with three bulbs is used. From 50 c.c. of the oil to be examined exactly 5 c.c. are distilled. A few drops of water pass over first and render the distillate turbid. These can be removed by shaking with anhydrous sodium sulphate. After filtration the distillate is examined in a 50 mm. polariscope tube, the temperature having been observed accurately. The result is computed for 20° in accordance with the directions given in footnote 1 on page 22 and deducted from the result obtained for the original oil likewise computed for 20°.[2]

In certain instances, more particularly when the amount of available oil is but small, the modification of Soldaini and Bertè is preferable. This consists in distilling off one-half from 25 c.c. of oil. In the case of pure oils, the optical rotation of the 50 per cent of distillate is higher than that of the original oil, likewise than that of the residue. In the case of adulteration with turpentine oil, that of the first half is invariably lower.

This modification, however, is no better than the original Schimmel test which, in an emergency, can be conducted with 25 c.c. of oil. For

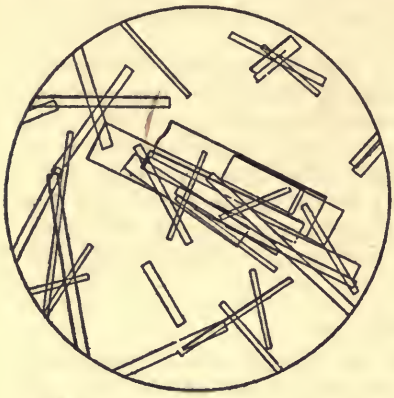
[1] In one instance, Chace observed as high as 6.17°.

[2] *Report of Schimmel & Co.* (October, 1896), p. 39.

the detection of the addition of lemon-oil terpenes both methods fail.[1] The suggestion made by Burgess to distil under diminished pressure does not afford any particular advantages.

DETECTION OF PINENE ACCORDING TO CHACE

Assuming that pure turpentine oil is at most to contain but traces of pinene, Chace[2] published a method for the detection of mere traces of turpentine oil. It is based on the observation that the nitrosochloride of pinene and limonene crystallize in different forms readily recognizable under the microscope. Whereas the pinene derivative separates in laminae, the limonene derivative crystallizes in needles.



(E. M. Chace)

FIG. 6.—Limonene nitrosochloride crystals from lemon oil.

Chace proceeds in the following manner: From 50 c.c. of oil contained in a Ladenburg flask, he fractionates 5 c.c. From this, with the aid of ethyl nitrite, he prepares the nitrosochloride according to Wallach's method. The reaction mixture is allowed to remain fifteen minutes in the freezing mixture when the crystals are removed by means of a suction filter, and washed with 50 c.c. of 95 per cent alcohol. The mother-liquid is exposed another fifteen to twenty minutes to the temperature of the freezing mixture. The second crop of crystals is united with the first. The united crystals are washed well with alcohol, dried, and dissolved in the smallest possible amount of chloroform. Enough hot methyl alcohol is then added to result in crystallization upon cooling. Finally somewhat more methyl alcohol is added and the crystals removed by filtration. For testing under the microscope, the crystals are best mounted in olive oil. In this manner Chace could detect an addition of 2 per cent of turpentine oil whereas with the aid of a three-

(E. M. Chace)

FIG. 7.—Limonene and pinene nitrosochloride crystals from a lemon oil mixed with 5 per cent of turpentine.

[1] Cf. also Bertè, *Boll. Chim. Farn.* (May, 1914), No. 10; *Report of Schimmel & Co.* (October, 1904), p. 29. *Chemist and Druggist*, LXVI (1905), 713.

[2] *Journal of the American Chemical Society*, XXX (1908), 1475; *Report of Schimmel & Co.* (October, 1908), p. 64. "The Occurrence of Pinene in Lemon Oil," *Bureau of Chemistry, United States Department of Agriculture Circular 46* (October, 1909).

(E. M. Chace)

FIG. 8.—Pinene nitrosochloride crystals from turpentine.

bulb Glinsky fractionating column even 0.5 per cent of added turpentine oil could be detected. Additions of 10 to 15 per cent could be detected by preparing the nitrosochloride from the original oil.

Both Umney and Parry have protested against the usefulness and applicability of this method. Wiley, however, justifies it by the claim that since its application by the Bureau of Chemistry of the United States Department of Agriculture not a single imported oil has had to be questioned.

It is necessary, however, to follow the directions. In the case of the isolation of but small amounts of pinene nitrosochloride, the oil should be allowed to pass and questioned only when larger amounts are obtained.

PATANÈ'S METHOD FOR DETERMINING THE AMOUNT OF THE CONSTITUENTS SOLUBLE IN DILUTE ALCOHOL

As is well known, lemon oil consists largely of terpenes and sesquiterpenes which are of but little value so far as the odor is concerned. Whereas these hydrocarbons are all but insoluble in 80 per cent alcohol, the valuable odoriferous constituents are soluble therein. Hence, Patanè regards the determination of the solubility as a valuable criterion in judging an oil and has based thereon a method of examination.

Indeed, he employs two methods. The one consists in shaking thoroughly equal volumes of oil and alcohol of definite strength measured at exactly 20° in a 10 c.c. cylinder graduated into 0.1 c.c. After the two layers have separated, the increase in the volume of the alcoholic solution is noted. According to the other method, equal volumes of the oil and alcohol of definite strength are mixed in a test tube, and gently heated until solution has taken place. The solution is then allowed to cool, being constantly stirred with a thermometer, the scale of which is divided into tenths of degrees. As soon as the solution becomes turbid, the temperature is read off. Differences in temperature of one-tenth degree produce turbidity. All oils that reveal the same turbidity temperature show the same solubility according to the first method, hence a comparative scale between turbidity temperature and solubility can be prepared. In most instances it suffices to carry out the second test which is said to be rapidly executed and yet exact.

The addition of 10 per cent of terpenes increases the turbidity temperature by more than one degree, that of 20 per cent about two degrees, etc., with this difference, however, that with the increasing terpene content, the temperature intervals become smaller. In addition, the relation

between citral content and solubility is said to admit of further conclusion as to the nature of the oil.

The alcohol used for this purpose must be standardized very carefully for the turbidity temperature varies with a difference in the strength of the alcohol of one-tenth of a degree. According to Patanè it is more expedient to use methyl alcohol in place of ethyl alcohol, since the oil is less soluble in the former. Inasmuch as the turbidity temperature in this instance lies above room temperature it is not necessary to cool the solution artificially as has to be done when ethyl alcohol of 93 to 94 per cent strength is used.

Both tests can also be applied advantageously to the oils of orange and mandarin which are much less soluble than lemon oil.

In the determination of the solubility it is necessary to consider the geographic source of the oil since oils from different localities vary in composition.

In order to judge the usefulness of this method more detailed experiments are necessary.

VISCOSITY DETERMINATION

According to Dowzard the viscosity of the volatile oils is said to be an important aid in the determination of the purity or quality of volatile oils. Inasmuch as it seemed highly desirable to increase the means of ascertaining the value of lemon oil, a number of viscosity determinations were carried out in the laboratory of Schimmel.[1] These are recorded in Table II. The apparatus used was the same employed by Dowzard, viz., the viscosimeter of Reischauer. As unit of viscosity the time of flow of 25 c.c. of water at 20° is indicated as 100. The viscosity number of the lemon oils tested is computed with the aid of the following formula:

$$V = \frac{O}{W} \times 100$$

where O = the number of seconds required by the flow of 25 c.c. of oil at 20°, and W = the number of seconds required by the flow of 25 c.c. of water at 20°.

So far as lemon oil is concerned, the experiments yielded no encouraging results. This is more particularly true of the addition of "citrene," for the values for "citrene" and lemon oil are too close to admit of the detection of this adulterant. Moreover, the difficulty of establishing standards is increased by the circumstance that different viscosimeters of the same make do not yield the same results, hence are not comparable. Whereas Dowzard found the viscosity number for pure lemon oil to be 139.6, the values found by Schimmel varied between 109.8 and 122.9. For "citrene" Dowzard found 105.8, Schimmel found 103.2.

The cause for these differences is to be looked for in the fact that the orifices of viscosimeter of this type are different. It may be possible to secure better results with more exact instruments that guard against this error. Quercigh and Moreschini regard the viscosimeter of Scarpa as

[1] *Report of Schimmel & Co.* (April, 1901), p. 32.

suited for the determination of the viscosity of volatile oils. Another advantage of this instrument lies in the fact that smaller amounts of oil (1 to 5 c.c.) suffice for the determination of exact results.

The results obtained by Schimmel & Co. are recorded in Table II.

DETERMINATION OF THE HYDROCARBON CONTENT OF CONCENTRATED LEMON OILS ACCORDING TO E. BÖCKER

This method consists in the removal, first of the citral by means of sodium sulphite, and then of the other aromatic substances by means of alcohol. The strength of the latter is chosen so that, with the observation of certain precautions, the hydrocarbons remain undissolved almost entirely. Böcker proceeds in the following manner:

The citral content of 10 c.c. of oil is first examined according to the sulphite method. If the volume of oil that does not enter into the reaction amounts to less than 6 c.c. the assay is repeated with either 5 or 10 c.c.

TABLE II

Origin of the Oil	$d_{15°}$	$\alpha_{D20°}$	Viscosity at 20° (Water=100)
Messina I	0.8576	+61°10′	120.0
Messina I hand pressed	0.8572	+60°18′	109.8
Messina I hand pressed	0.8594	+61°57′	144.6
Messina I machine pressed	0.8574	+61° 4′	122.9
Messina I hand pressed	0.8565	+61°27′	111.3
Messina I hand pressed	0.8568	+61°32′	112.0
Messina I hand pressed	0.8583	+62°10′	111.3
Palermo I	0.8592	+60°20′	117.0
Palermo II	0.8591	+59°12′	121.0
Messina II	0.8568	+61°28′	113.6
Citrene from lemon oil:			
From Palermo	0.8533	+65° 6′	103.2
From Messina	0.8514	+66°35′	102.1
d-Limonene, crude	0.8528	+101°35′	100.9
Limonene, pure	0.8470	+117°40′	100.2
Citral, fresh	0.8932	±0°	201.4
Citral, old	0.8967	±0°	207.8

The non-aldehyde constituents of both assays are united and 5 c.c. thereof transferred to a 600 to 700 c.c. separating funnel into which 500 c.c. of 51 per cent alcohol (by volume), cooled to from 0 to —2°, have previously been placed. The separating funnel is stoppered with a cork and the contents are shaken repeatedly thus causing the aromatic constituents to go into solution, whereas the hydrocarbons remain undissolved almost quantitatively. The inverted separating funnel (stopper downward) is then transferred to a bath of 0° in which it is allowed to remain for eight to

ten hours. After this time it is removed, carefully brought back to its normal position and suspended from a ring stand. After the alcoholic solution has become so clear that but a very faint turbidity remains, which may require up to two days, all but about 10 c.c. of the liquid are drawn off. Any oil drops adhering to the separating funnel are washed down with ice-cold 50 per cent (no doubt should read 51 per cent) alcohol so that all dissolved oil is brought together. The separating funnel is again set aside until the alcohol has become well-nigh perfectly clear. After the last traces of alcohol have been separated so far as this is possible, the oil is transferred to a measuring cylinder, graduated into one-tenth cubic centimeters, the separating funnel being again rinsed with some ice-cold 51 per cent alcohol. It is more practicable to use a separating funnel, the lower portion of which is drawn out to a narrow, calibrated tube. As soon as the oil has become clear (in case foam persists a few drops of dilute acetic acid are added), its volume is read off and the percentage with reference to the original oil computed.

If larger amounts of material are available, the quantitative determination can be supplemented by a qualitative examination of the separated hydrocarbons. For this purpose Böcker provides the following directions: 100 to 200 c.c. of oil are fractionated in vacuum. The distillation is continued only so far as the fractions of 10 c.c. each reveal dextrorotation. These are united as the terpene-containing portion of the oil whereas the remainder constitutes the sesquiterpene-containing portion of the oil. Both of these portions are now deprived of citral by means of sodium sulphite. The residual oils are treated separately as described above, with 100 times their volume of ice-cold 51 per cent alcohol. If desired, glass bottles can be used in the place of the separating funnels, the alcohol being removed by means of a siphon. The separated oils are measured and the terpene and sesquiterpene contents of the original oil computed. For further identification the optical rotation is ascertained and the characteristic derivatives are prepared. The terpene fraction on the one hand, consisting principally of *d*-limonene, is characterized by strong dextrorotation, and affords a good yield of limonene tetrabromide. The sesquiterpene fraction, consisting principally of bisabolene, is laevogyrate and can be further characterized by the bisabolene trihydrochloride.

Böcker has tested his method in connection with a number of experimental mixtures and obtained good results. In connection with a terpene-free lemon oil produced by himself, he obtained 51.5 per cent of citral and 21 per cent of hydrocarbons. In connection with a terpene- and sesquiterpene-free oil, also produced by himself, he found 62 per cent of citral and traces of hydrocarbons too small in amount to be measured. In terpene-free lemon oils he regards a 25 to 30 per cent hydrocarbon content as normal.

A comparison of the citral and hydrocarbon contents is said to enable the detection of the addition of lemon-grass citral to a concentrated oil. Tests made with two oils, to which 20 per cent of citral had been added, revealed that the exact amount of the addition could not be proved, but that only one-half thereof was indicated. Nevertheless, the minimum of adulteration can be recognized.

For the purpose of valuation, Böcker proceeds from the consideration that a lemon oil, freed entirely of its hydrocarbons, contains a maximum of 66 per cent citral. This leads to the results in Table III.

TABLE III

Hydrocarbon Content (Per Cent)	Highest Admissible Citral Content (Per Cent)	Hydrocarbon Content (Per Cent)	Highest Admissible Citral Content (Per Cent)
0	66	30	46.2
3	62.7	35	42.9
10	59.4	40	39.6
15	56.1	45	36.3
20	52.8	50	33
25	49.5		

This table can be supplemented as desired, since for every 1 per cent of hydrocarbon 0.66 per cent citral should be deducted. Hence, in passing judgment on a concentrated oil, Table III should be consulted to ascertain whether the hydrocarbon content agrees with the citral content. If the oil in question contains more citral than is usual according to this table, this may be regarded as adulteration with added citral. In order to ascertain the minimum amount of added citral, the maximum citral content corresponding to the hydrocarbon content, as shown in the table, is noted. This amount of natural citral is deducted from the citral found by the sulphite assay. The difference stands for the minimum amount of citral added.

The details of the computation can be explained better with the aid of data supplied by Böcker. Having ascertained the presence of 15 per cent of hydrocarbon and 61 per cent of citral, Table III reveals that these values do not correspond, since according to Böcker the citral content of an oil containing 15 per cent of hydrocarbon should not exceed 56 per cent. Hence citral from another source must have been added. Inasmuch as a normal with 56 per cent citral should contain $100 - 56 = 44$ per cent of non-citral, and since the examined oil contains only $100 - 61 = 39$ per cent of non-citral, the normal citral content of the latter is revealed by the following equation: $44 \cdot 56 = 39 \cdot x$; when $x = 49.63$. This number corresponds to the highest lemon oil citral content of an oil containing 39 per cent of non-citral. Inasmuch, however, as 61 per cent have been found, an adulteration with at least $61 - 49.63 = 11.37$ per cent of foreign citral may be assumed.

Whether this method is of general application to all concentrated oils produced by different methods can be ascertained only by experiment. It is noteworthy that, according to the method of production, other constituents than the hydrocarbons may be removed from the original oil. This may result in an increased citral content of the concentrated oil. Hence, a high citral content may not invariably indicate adulteration.

ADULTERANTS

Twenty-five years ago, when the constants of pure lemon oil were not known and when the polariscope was not utilized in its examination, French and American turpentine oil[1] were the common adulterants. After the introduction of the polariscope method, the adulterators took recourse to mixtures of turpentine oil with carvene, orange oil terpenes, or distilled lemon oil. Later, when the production of terpene-free lemon oil came into vogue, the citrene, resulting as waste product, became the most favored and dangerous adulterant, for its detection, like that of citral from lemongrass oil, is exceedingly difficult. Of adulterants that can be detected readily, the following have been observed: cedarwood oil, stearin,[2] mineral oils, alcohol,[3] castor oil[4] and finally mixtures of alcohol and glyceryl acetate.[5]

OIL OF LIMES

Two oils coming from different plants (*Citrus aurantifolia* (Christm.) Swingle and *C. limetta* Risso) and of entirely different properties are designated by the common name of limette oil,[6] but according to their source may be called West Indian and Italian limette oils.

They are obtained either by an expression process (generally by the écuelle) or by distillation. The pressed oil is the superior of the two and commands a much higher price.

WEST INDIAN LIMETTE OIL

The West Indian oil, which is the usual oil of commerce, is obtained from the fruits of *Citrus aurantifolia,*[7] the juice of which contains a large quantity of citric acid. The plant is plentiful in Jamaica, Dominica, and Tahite; but the most important plantations are on the island of Montserrat, one of the Antilles. The lime harvest there lasts from September to January, and the chief product is, of course, the lime juice.

The oil obtained from the peel of the fruit by expression (oil of limette) is of a golden-yellow color and can hardly be distinguished from a good lemon oil by its odor, if the[8] greater intensity of that of

[1]More recently the strongly dextrogyrate Greek oil is being used for this purpose. E. J. Parry, *Perfumery Record,* II (1911), 209.

[2]G. Boswigi, *Chemist and Druggist,* LV (1899), 710.

[3]*Report of Schimmel & Co.* (April, 1908), p. 45.

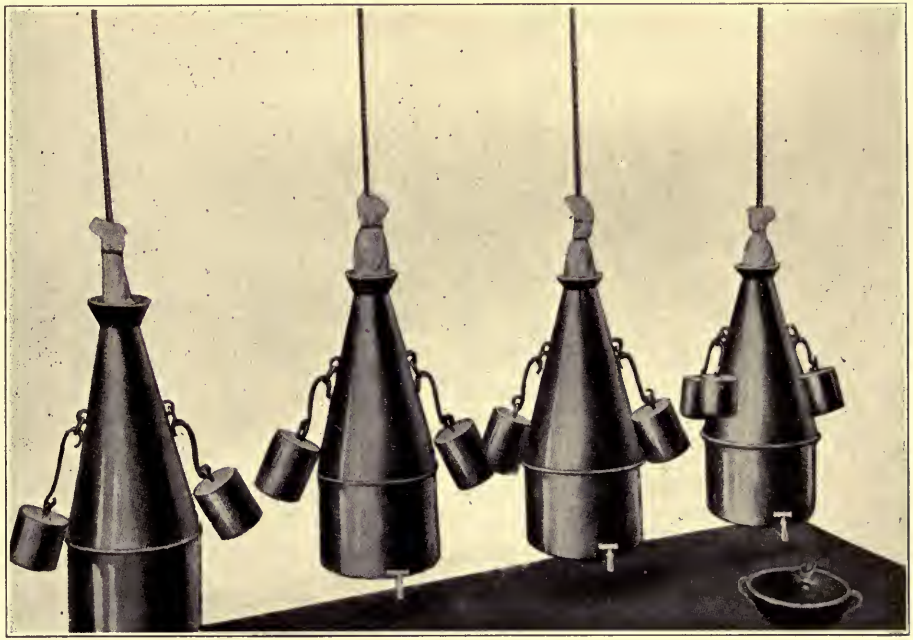
[4]E. J. Parry, *Chemist and Druggist,* LXXIV (1909), 121.

[5]*Report of Schimmel & Co.* (April, 1913), p. 61.

[6]*Archiv der Pharmazie,* CXXXIII, 174.

[7]*Bulletin of Miscellaneous Information, Royal Gardens Kew* (1894), p. 113.

[8]*Pharmaceutical Journal,* III, No. 15, 322.



(Roure-Bertrand fils)

FILTERING APPARATUS FOR THE OIL OF BERGAMOT.

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the limette oil is not considered. Specific gravity 0.873 at 29° to 0.882 at 15°; α_D +35° to +38°. The most important constituent of the oil is citral.

Entirely different from the expressed oil is the distilled oil which is obtained as a by-product in the evaporation of the juice and is known in commerce under the name of oil of limes. Its odor is unpleasant, terebinthinate, and no longer reminds of citral. Probably this aldehyde is completely destroyed by the boiling of the acid liquid.

Tempany and Greenhalgh, who have investigated the matter, are of opinion that the difference is caused by the loss, during the process of distillation, of part of the lowest and highest boiling fractions. They distilled hand-expressed oils with steam, and obtained an oil with the characteristic turpentine-like odor of the distilled oil of commerce. The highest boiling fractions of the hand-expressed oil contain a blue fluorescent, crystalline body (perhaps methyl anthranilate), which is absent from the distilled oil. Moreover, limettin, which ordinarily separates out from the hand-expressed oil when it is left standing, is absent from the distilled oil. As a rule the citral content of the distilled oil is lower than that of the hand-expressed oil. The authors mentioned found authentic samples to show the following properties:

I. Hand-expressed oils: specific gravity, at 30° 0.8712 to 0.8859, α_D31° +31°38′ to +33°43′, specific gravity at 32° 1.4789 to 1.4851, acid value 1.35 to .8, citral content 2.2 to 6.6 per cent.

II. Distilled oils: d30° 0.8540 to 0.8858, α_D31° +33°09′ to 34°89′, $n_{D32°}$ 1.4702 to 1.4713; acid value 0.76 to 1.3, citral content 1.2 per cent to 2.0 per cent.

ITALIAN LIMETTE OIL[1]

The fruit of the South European limette, *Citrus limetta* Risso (*Lima di Spagna dolce, Limettier ordinaire*) is distinguished from that of the West Indian by its sweet juice.

Italian lime oil obtained by expression from the peel, is of a brownish-yellow color and has a characteristic fragrant odor of the fruit with a secondary odor of bergamot. It forms a yellow deposit of limettin in considerable amounts on standing. Its specific gravity varies from 0.870 to 0.875, its saponification number is 75 and its rotation from +34° to +40°. It contains linalyl acetate and citral. It also contains a little free linalool, but not more than 3 or 4 per cent. The bulk of the oil consists of the terpene limonene.

The composition of the Italian limette oil is very similar to that of bergamot oil, only the limette oil contains more limonene and less linalyl acetate.

[1] *Ibid.*, III, No. 14, 1005; Gildemeister.

The limonene is the dextrogyrate modification (α_D +81°45′; specific gravity 0.848) and yields a dihydrochloride melting at 50°, as well as a tetrabromide melting at 105°.

In the oil investigated by Gildemeister[1] 26.3 per cent of linalyl acetate were present (boiling-point 101°–103° at 13 mm.; specific gravity at 15° 0.898; α_D—9°52′).

After saponification with alkali, acetic acid was found in the alkaline solution, while from the oil *l*-linalool (boiling-point 88.3°–89.5° at 13 mm.; specific gravity at 15° 0.870, (α_D —20°7′) was separated by fractional distillation. From it citral was formed on oxidation.[2] Linalool is present in the oil partly in the free state, partly as acetic acid ester.

The limettin which separated from the oil on standing melts according to Tilden at 121°–122°. It has the composition $C_6H_3(OCH_3)_2 \cdot C_3HO_2$ and yields on melting with potassium hydroxide, besides acetic acid, phloroglucin.

OIL OF MANDARINS

Origin.—The peel of the fruit of *Citrus nobilis* Loureiro,[3] known as mandarins, contains a very pleasant-smelling oil which is obtained, like the oils of the other agrumen fruits, by expression.

Properties.—Mandarin oil is a golden-yellow liquid with a slight bluish fluorescence (probably due to methyl anthranilate), which becomes more prominent when the oil is diluted with alcohol. The odor, although resembling that of lemon oil, is more pleasant and distinctly different from it. $d_{15°}$ 0.854–0.858; α_D +65° to +75°.

α_D of the first 10 per cent of distillate is (cf. under Oil of Lemon, p. 29) slightly lower or but 2 per cent higher than that of the original oil. According to E. Bertè and G. Romeo the α_D of the first 50 per cent should average 3° higher than the original oil; $n_{D20°}$ 1.475 to 1.478; acid valuation up to 1.7; ester valuation 5 to 11; ester valuation after acetylation 12.5 (1 determination); evaporation residue 2.4 to 3.5 per cent; soluble in 7 to 10 volumes of 90 per cent alcohol with more or less turbidity.

A Spanish oil from the province of Valencia, which had been expressed from the immature fruits, had an olive-green color and an agreeable odor, but less delicate than that of the oil from ripe fruits. Its physical constants also revealed deviations: $d_{15°}$ 0.8665; $n_{D20°}$ 1.47900; acid valuation 0.2; ester valuation 17.3; evaporation residue 8 per cent. On account of the dark color, the angle of rotation of the original oil could not be observed. The first 10 per cent of the distillate showed α_D +55°12′. In

[1]The same dihydrochloride was obtained by de Luca in 1860 (*Comptes Rendus*, LI, 258) from the terpene boiling at 180° of an oil, which is designated as coming from *Citrus lumia*, but which in all probability was Italian limette oil. Cf. Gildemeister, *loc. cit.*

[2]To which compound the "limettsaure" $C_{11}H_4O_6$ obtained by Vohl in 1853 upon the oxidation of the oil (*Archiv der Pharmazie*, CXXIV, 16) owes its origin, is uncertain.

[3]According to de Lucca the mandarin is obtained from *Citrus bigaradia sinensis* and *C. b. myrtifolia.*

90 per cent alcohol the oil was not completely soluble, but it formed a clear solution with 0.5 volume and more of 95 per cent alcohol.[1]

Two mandarin oils[2] distilled in Porto Alegra (Brazil) had the following properties: $d_{15°}$ 0.8515 and 0.8510; α_D +74°16′ at 17° and +75°20′ at 16°. Both oils were distinguished by a beautiful blue fluorescence.

Composition.—The greater part of distilled mandarin oil consists of *d*-limonene. Citral and citronellal are probably also present. The constituent to which the characteristic odor as well as the fluorescence is due is methyl anthranilic ester, present in a quantity of scarcely 1 per cent.

The expressed mandarin oil, according to Flatau and Labbe, contains the same ester as does orange oil.

d-Limonene. The oil began to boil at 175° and all except a small residue went over up to 179°. The fraction boiling at 175°–177° (α_D +76°45′) gave on bromination in glacial acetic acid solution a tetrabromide melting at 104°–105° (Gildemeister and Stephan, 1897). By conducting hydrochloric acid into the same fraction dipentene dihydrochloride, melting-point 49°, resulted (de Luca, 1857). According to this *d*-limonene was present in large quantity.

Citral and citronellal. If the portion which did not distil over up to 177° be treated with bisulphite solution, an addition product is obtained from which an oil is separated by alkali. This behaves like a mixture of citral and citronellal when condensed with pyrotartaric acid and β-napthylamine. The melting-point of the naphtho-cinchoninic acid formed is not constant. At 197° (the melting-point of the pure citral compound) the body begins to run together, but does not melt completely until 222° (melting-point of the citronellal compound 225°). The positive identification of these two aldehydes in the oil has, therefore, not yet been made.

Methyl anthranilic acid methyl ester. This substance was found by Walbaum in 1900. From 5 kg. of mandarin oil 36 gm. of a base were obtained by shaking with the sulphuric acid, the bulk of which distilled between 130° and 131° (13 mm.). Its specific gravity was 1.120 at 15°. In the cold it congealed and melted at 18.5° to 19.5°. This compound forms salts and double salts and its odor is similar to that of anthranilic acid methyl ester. When heated with hydroiodic acid it decomposes with the formation of methyl iodide. Alcoholic potassium hydroxide saponifies the ester and from the salt solution acetic acid precipitates the methyl anthranilic acid.

This acid melts at 179°. When heated with dilute hydrochloric acid to from 160° to 170° it decomposes into carbonic acid and methyl aniline. It yields the same derivatives obtained by G. Fortmann from the synthetic methyl anthranilic acid, e.g., nitrosomethylanthranilic acid (melting-point 128°), acetylmethylanthranilic acid (melting-point 186°) and benzoylmethylanthranilic acid (melting-point 161°).

[1] *Report of Schimmel & Co.* (October, 1911), p. 46.
[2] *Report of Schimmel & Co.* (April, 1896), p. 62.

Synthetically the methyl ester of methylanthranilic acid

$$C_6H_4<\begin{matrix}NH\cdot CH_3[1]\\COOCH_3[2]\end{matrix}$$

can be obtained by boiling the methyl alcoholic solution of methylanthranilic acid with sulphuric acid and subsequent decomposition of the ester salt with soda solution.

Quantitatively (Hesse and Zeitschel) the amount of ester can be determined as its anthranilic acid methyl ester.

JAPANESE MANDARIN OIL

Three samples of mandarin oil of Japanese origin, are reported upon in 1914. As they were colorless, it was evident that these oils had not been obtained by pressure, as is the custom in Italy, but by distillation. Consequently they were devoid of the fine aroma of the Italian oils, but smelled chiefly of limonene and, therefore, did not compete with genuine mandarin oils. The method of production is illustrated by the chemical constants, as specified in Table IV.

TABLE IV

	$d_{15}°$	α_D	α_D of the First 10 per cent of the Distillate	Acid Value	Ester Value	Solubility in 90 per cent Alcohol
I.....	0.8489	+92°35′	+91°32′	0.3	3.7	5.5 vol. and more
II.....	0.8528	+73°36′	+66°10′	0.3	3.6	5.5 vol. and more
III.....	0.8541	+68° 5′	+60°48′	0.3	4.6	5 vol. and more

Three oils sent to Schimmel & Co.[1] under the name of Mikan oil were evidently also mandarin oils, for the mandarin fruit is called "Mikan" (Rein) in Japan. These oils showed somewhat similar constants to the above-mentioned distillates:

$d_{15°}$ 0.8483; α_D+92°20′; soluble in 6 volumes and more of 90 per cent alcohol.

$d_{15°}$ 0.8478; α_D+90°56′; soluble in 6.2 volumes and more of 90 per cent alcohol.

$d_{15°}$ 0.849 ; α_D+90°35′; soluble in about 10 volumes and more of 90 per cent alcohol.

The values of Italian mandarin oil are within the following figures: $d_{15°}$ 0.854 to 0.859; α_D +65° to +75°; α_D of the first 10 per cent of the distillate very little lower, or even up to 2° higher than the original oil acid value up to 1.7; ester value 5 to 11; more or less turbidity when dissolved in seven to ten volumes of 90 per cent alcohol.

An English journal (*Perfumery Record,* V [1914], 721) also reports on a mandarin oil of Japanese origin. This oil had been obtained by distillation and was of a very fine odor; it showed a specific gravity of 0.848 and a rotation of +94°. A slight fluorescence noticed in this oil is put

[1]*Report of Schimmel & Co.* (October, 1914—April, 1915), pp. 18-23.

down by the author to the presence of methyl ester of anthranilic acid. We may be permitted to point out that, according to our observations, this latter body is not present in mandarin oil, but the methyl ester of methyl-anthranilic acid, which may well be the cause of the fluorescence observed in the oil in question.

OIL OF SWEET ORANGE

Botanically the sweet orange is *Citrus sinensis* (L.) Osbeck. Like lemon oil, this oil is obtained by expression, both in Sicily and Calabria. In recent years occasional samples have reached Europe from the West Indies. Likewise, as with lemon, the attempt has been made in California to obtain a so-called "oleoresin" by means of extraction with volatile solvents.

Properties.—Oil of orange is a yellow to yellowish-brown liquid of a characteristic orange odor and a mild, aromatic, not bitter taste. Specific gravity at 15° 0.848–0.852; α_D +96° to 98° at 20°.[1]

On account of the presence of waxlike, non-volatile substances of unknown composition, which partly separate on standing for some time, the oil as a rule does not form a clear solution with 90 per cent alcohol. It begins to boil at 175°; up to 180° nine-tenths distil over.

The rectified oil is colorless; its specific gravity is somewhat lower, the rotatory power slightly higher than that of the original oil. Rectified orange oil is kept with difficulty, it deteriorates rapidly, and acquires thereby a stale, unpleasant odor.

The oil yields a clear solution with about one-fourth to one-half volume of 90 per cent alcohol and the solution does not become turbid on the addition of more alcohol. All oils do not dissolve clearly in 80 per cent alcohol. Many, and especially those of a high ester content, often give turbid mixtures, from which fatty globules separate on the bottom.

The following constants were observed in connection with several oils from Jamaica: $d_{15°}$ 0.8481 to 0.8491; $\alpha_{D20°}$ +97°43′ to +98°2′; α_D of the first 10 per cent +96°32′ to +97°30′; $n_{D20°}$ 1.46984 (1 determination); decylic aldehyde 2.3 to 3.8 per cent; evaporation residue 1.4 to 2.0 per cent.

An oil from Dominica[2] had the following constants: $d_{15°}$ 0.8486; $\alpha_{D20°}$

[1]Since the angle of rotation of orange oil like that of lemon oil varies greatly with changes in temperature, decreasing with an increase in temperature, it is necessary in order to obtain comparable numbers, to ascertain accurately the temperature and to reduce the result to 20° by calculation. As the difference in the angle of rotation between +10° and +20° is 14.5 minutes and between +20° and +30° it is 13.2 minutes for one degree of change in temperature, the reduction to 20° is made by deducting 14.5 minutes for each degree of temperature, when the polarization was effected at a temperature below 20°. If the determination was made at a temperature above 20°, 13.2 minutes are to be added to the number found in order to find the angle of rotation of +20°.

[2]Examined in the laboratory of Schimmel & Co.

98°21′; α_D of the first 10 per cent 97°40′; evaporation residue 1.6 per cent, with saponification value 171.5.

In connection with three samples of oleoresin of orange the following constants were observed: $d_{15°}$ 0.8535 to 0.8723; $\alpha_{D20°}$ about +75° to +89° (an approximate determination only was possible because of the dark-brown color of the preparation), α_D of the first 10 per cent +90°54′ to +96°26′, evaporation residue 11 to 14.7 per cent, acid value of the residue 13.5, ester value 107.0 to 112.0.

Properties of the terpenes from orange oil: $d_{15°}$ 0.847 to 0.854; α_D +95°50′ to +100°18′; $n_{D20°}$ about 1.473; soluble in 8 to 9.5 volumes of 90 per cent alcohol, with partial turbidity.

Composition.—Orange oil contains *d*-limonene, aldehydes—citral, citronellal and possibly others of unknown composition—methyl ester of anthranilic acid and stearoptene.

Wallach (1884) has shown the presence of at least 90 per cent of *d*-limonene (dihydrochloride, melting-point 50° (Soubeiran and Capitaine[1]) (1840), tetrabromide, melting-point 104°–105°). On this account, especially as other hydrocarbons are completely absent, it is well suited for the preparation of this terpene in a pure state. The absence of pinene is of importance for the detection of adulteration with turpentine oil.

Aldehydes. Of oxygenated compounds, aldehydes are present in orange oil. By shaking with sodium bisulphite solution, crystals of a double compound are formed, which can be isolated by filtration and pressing; by decomposing with soda an oil is obtained which is purified by steam distillation. A part of this boils at 224°–228° and consists of citral (Semmler, 1891). The lower boiling fraction likewise contains an aldehyde, the composition of which has not yet been determined.

The assertion made by Wright in 1873 that oil of orange peel contains 0.3 per cent of a body boiling at 212°–218° identical with myristicol ($C_{10}H_{16}O$) of the oil of nutmeg, is too little supported by facts.

The most recent investigation of orange oil is that of Flatau and Labbe. They obtained by shaking orange oil with bisulphite solution a double compound which yielded besides traces of citronellal, a small amount of a new aldehyde that had a very characteristic orange color. In addition an acid of possible twenty-one carbon atoms was isolated. Like the acid, its ethyl ester is difficultly soluble in alcohol and can be precipitated by this solvent from the residue of the oil after 95 per cent have been distilled off. When purified it melts at 64°–65° and has a pleasant and characteristic orange odor.

Methyl ester of anthranilic acid. Parry suspects the presence of the methyl ester of anthranilic acid in sweet orange oil. This observation is confirmed by Schimmel & Co.[2] who have definitely shown its presence.

Stearoptene. Of the nature of the orange oil stearoptene, which finds its way into the oil by expressing the peel of the fruit and which remains in the residue when the oil is rectified, nothing is known.

[1]Cf. also Vöchel, *Liebigs Annalen der Chemie*, XXXIX (1841), 120; and Wright and Piesse, *Chemical News*, XXIV, 147; *Chem. Zentralblat* (1871), p. 740.

[2]*Report of Schimmel & Co.* (April, 1900), p. 18.

Examination.—On account of the low specific gravity and the extraordinarily large rotatory power of orange oil, all kinds of foreign additions can be readily and accurately detected, as there is no adulterant by which these two properties would not be changed.

Formerly, when the polariscope was not so generally used as it is today the oil was greatly adulterated with turpentine and sometimes even with lemon oil.

The terpenes remaining from the manufacture of terpene-free lemon oil were used to an enormous extent in Messina for the adulteration of orange oil.[1]

For the detection of turpentine oil the lowest boiling portions of the oil are repeatedly fractionated by employing a dephlegmator, and the pinene may then be recognized by its boiling-point, as well as by its rotatory power (strongly laevogyrate with French and slightly dextrogyrate with American turpentine oil). Should such a test be considered as not conclusive, the pinene must be converted into pinene nitrosochloride and into the characteristic pinene nitrolbenzylamine or nitrolpiperidine base.

The decylic aldehyde content can readily be determined by means of phenylhydrazine. The method to be employed is the same as that used for the citral assay in lemon oil (cf. p. 64) with this difference that the mixture of orange oil and phenylhydrazine solution should be allowed to stand for two hours. Decylic aldehyde reacts slower than does citral so that complete reaction is not assumed within less time. With mixtures of decylic aldehyde of known content, there have been obtained very satisfactory results in this manner. Poorer results are, in turn, obtained by prolonging the reaction time beyond the two hours. According to observations made thus far, the decylic aldehyde content of oil of orange varies between 1.3 and 2.7 per cent.

A sweet orange oil examined by Schimmel in 1917, is worthy of mention and may serve as a warning. It was quite sufficient to determine its specific gravity and optical qualities, in order to form an opinion on its quality. The constants indicated were as follows: $d_{15°}$ 0.8662; $\alpha_{D25°}$ +58°18′; α_D of the first 10 per cent of the distillate +56°20′. Compare with this the characteristics of genuine sweet orange oil, namely, at 15° a specific gravity of 0.848 to 0.853 and an optical rotation of +95°30′ to +98°; the first 10 per cent of the oil has a rotation not measurably less than the original oil.

The extreme divergence from the normal figures makes it quite obvious that the sample was at least greatly adulterated. Probably, however, this was an artificial product in which lemon oil terpenes had been employed, whereas orange oil is entirely absent, which can be inferred by the exceedingly low degree of rotation of the first 10 per cent of the distillate (boiling over 172°). However, there is no doubt that this was a case of fraud.

Hood publishes an account of the oil content of Florida oranges. At various periods he collected oranges during harvest time and made a determination of the oil value of the peel. Thereby the fact came to light that conditions of climate and culture greatly influence the oil

[1] *Ibid.* (October, 1899), p. 25.

content of the fruit which besides varies considerably with the species. Only when fully ripe does the peel contain its highest percentage of oil, which is, however, sufficiently abundant to permit of collecting even in unripe fruit which is seldom gathered. Rain during harvest reduces the oil yield considerably. The occurrence of a rust mite has no effect on the oil yield of the ripe fruit. In tabulated form Hood reports on the weekly oil yield for eight orange varieties from seventeen different localities in Florida.[1]

JAMAICA SWEET ORANGE OIL

Specific gravity at 15° 0.8481 to 0.8491; α_D 20° +92°43′ to +98°3′; α_D of the first 10 per cent of the distillate +96°14′ to +97°30′, in every instance a little lower than the original oil; specific gravity at 20° 1.46984 (one test only; evaporation residue 1.4 to 2.0 per cent in three aldehyde determination carried out with phenylhydrazine 3), 2.3, 2.7, and 3.8 per cent respectively were found, calculated for decylic aldehyde.

OIL OF BITTER ORANGE

The oil of bitter orange (*Citrus Aurantium* L.), which plays only a subordinate rôle in commerce in comparison with oil of sweet orange, differs from this mainly in its bitter taste. The rotatory power[2] is sometimes slightly lower and varies from +92° to +98°.

All other properties are the same as those of the sweet oil, and it is impossible to distinguish between the two oils in any other manner than by their odor and taste.

ITALIAN BITTER ORANGE OIL

According to P. Fenaroli the bitter orange has for some time been made use of for the production of oil in Italy; he is of opinion that it may become an important article of commerce in future. The odor resembles ordinary lemon oil, but has a scarcely pleasant by-odor the elimination of which may possibly be attained in time. Fenaroli[3] gives the following figures for this oil: $d_{15°}$ 0.847 to 0.848; $\alpha_{D20°}$ +94°.10′ to +95°.40′; $n_{D17°}$ 1.47388 to 1.47408; not readily soluble in 80 per cent alcohol. Soluble in four to four and one-half volumes of 90 per cent alcohol. It boils at 80 mm. from 102° to 120° and contains 97 to 98 per cent of *d*-limonene, besides small quantities of *d*-pinene (?), as well as some bodies boiling above 176°. Citral could not be found.

[1] *Report of Schimmel & Co.* (April–October, 1917), pp. 16–17.

[2] *Ibid.* (April, 1896), p. 29.

[3] Compare *Report of Schimmel & Co.* (April, 1912), pp. 76, 77. Unlike experiments with the citral determination the oil is here allowed to be in contact with phenylhydrazin for two hours, experiments with decylic aldehyde solutions having shown what with a contact of one hour only the results obtained are too low.

WEST INDIAN BITTER ORANGE OIL

The *Journal of the Jamaica Agricultural Society* reports that before the great Messina earthquake West Indian orange oil was rarely to be found in the London market. After this catastrophe, however, more care was bestowed in Jamaica on the orange oil production which labors under some difficulties, inasmuch as the trees occur but singly, and not in groves, making the gathering of the fruit difficult. Armed with hand presses and bottles the farmers must proceed from tree to tree, collect the fruit, and peel it on the spot. The bottles are filled with a mixture of oil, vegetable slime, and juice. When settled, the oil is poured off into copper vessels. As the demand is but limited, steps are contemplated to avoid overproduction if possible.

JAMAICA BITTER ORANGE OIL

$d_{15°}$ 0.8517 to 0.8537; $\alpha_{D20°}$ +92°57′ to +96°58′; α_D of the first 10 per cent of the distillate +92°20′ to +96°40′, only in one instance higher than the original rotation; $n_{D20°}$ 1.47171 (one test only); evaporation residue 2.6 to 3.2 per cent. Aldehyde content 0.75 to 1.5 per cent, calculated for decylic aldehyde.

Two further orange oils, also originating from the West Indies, were submitted to Schimmel by the Imperial Institute of London. Both had been obtained by pressure, one from green, the other from yellow oranges. Unfortunately, the samples were so small that they were only sufficient for the determination of specific gravity and rotation. These values were within the recognized limits of sweet orange oil:

Oil from green oranges: $d_{15°}$ 0.8515; $\alpha_{D20°}$ +98°2′
Oil from yellow oranges: $d_{15°}$ 0.8492; $\alpha_{D20°}$ +97°22′

OIL OF CITRON

Origin.—According to Gullì the following citron varieties are cultivated in Calabria and Sicily: (1) *Citrus medica,* var. *vulgaris,* Risso, known in Calabria and in Sicily as "Cedro"; (2) *Citrus medica,* var. *gibocarpa* or *citrea,* Risso, designated "Cedrino"; (3) *Citrus medica,* var. *rhegina,* Pasquale, known by the name "Cedrone."

However, in commerce these three varieties of *C. medica* L. are not commonly differentiated. As a rule these fruits are not used for the production of volatile oil but, pickled in brine, they are exported, the one that is most sought being that designated "cedrone." Citron oil is produced by expression from the first two varieties, and then usually on request only at the time of harvesting the fruit in Sicily and in Reggio-Calabria. It is rarely found in a pure condition since the manufacturers add to it varying amounts of lemon or orange oils or the oil of the sweet lemon.[1]

[1]For an oil prepared from the "süsse Limone" Schimmel & Co. (*Report of Schimmel & Co.* [April, 1903], p. 39) ascertained the following constants: $d_{15°}$ 0.8579; $\alpha_{D20°}$ +64°15′; $n_{D20°}$ 1.47568. It smells of citral. According to E. Bonavia (*The Cultivated Oranges and Lemons of India and Ceylon* [London, 1888], p. 67), the parent plant of the "sweet lemon" is *Citrus Lumia,* Risso.

The oil of the "cedrone," does not appear to be known.

Properties.—Although the oils from the fruits known as cedro and cedrino are not kept separate in commerce, nevertheless they possess distinctive properties.

1. Oil of cedro or cedrat. $d_{15°}$ 0.8706 (Gullì) and 0.871;[1] a_D +67° (Gullì) and +67°8′.[2]

2. Oil of cedrino. $d_{15°}$ 0.854; a_D +77° to 81°; $n_{D20°}$ (one determination) 1.47519 (Gullì, 1903).

Composition.—An oil of cedro or cedrat has been examined by Schimmel.[3] Upon distillation the bulk of the oil passed over between 177° and 220°. The presence of citral was demonstrated by boiling with an alcoholic solution of β-naphthylamine and pyruvic acid, yellow crystalline laminae of citryl-β-naphthocinchoninic acid melting at 197° to 200° resulting.

Burgess (1901) has examined an oil which he regards as cedro oil, but which Gullì (1903) proved to be a cedrino oil. The bulk of the oil consisted of terpenes: according to Burgess mostly limonene with some dipentene (derivatives not mentioned). That portion of the oil which passes over between 64° and 85° under a pressure of 10 mm. contains citral. With cyanacetic acid it yielded citralidene cyanacetic acid. Determined according to the bisulphite method the citral content averaged 6 per cent, according to the hydroxylamine method 5.7 per cent.

In the bottle of the examined oil a deposit had been formed. By solution in chloroform a crystalline compound $C_{18}H_{18}O_6$ was isolated that melted at 145° and probably is identical with citroptene (cf., however, formula on p. 28).

OIL OF GRAPEFRUIT

Grapefruit, *C. maxima* Merrill, in common with all other citrus fruits may be made to yield an essential oil, but up to the present time grapefruit oil has not appeared in the trade. Experimentally it has been produced in small quantities, but in the presence of an abundant supply of lemon and orange oil no attempt appears to have been made to manufacture it on a large scale. Its production would doubtless be somewhat complicated by the presence of the bitter principle characteristic of this fruit.

Properties.—Odor, strongly that of citral; color, clear greenish yellow; refractive index at 20°C. 1.4750 and 1.4785; optical rotation in 100 mm. tube at 20°C. −72.5 and −78.5; specific gravity at 20°C., 0.845 and 0.860.

Composition.—In the oil analyzed tests were obtained for the presence of *a*-pinene, *d*-limonene, linalool, citral, and geraniol.

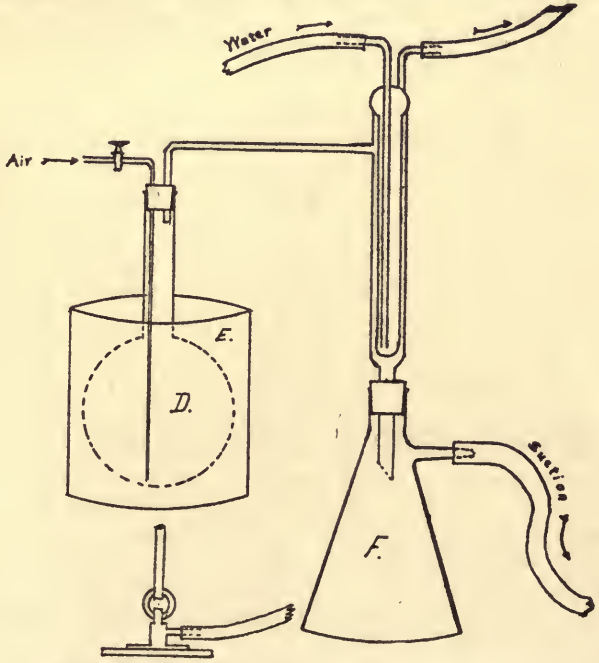
[1] *Report of Schimmel & Co.* (October, 1895), p. 13.
[2] *Ibid.*
[3] *Ibid.*

Large quantities of fresh peel representing the Indian River, DeSoto, and Excelsior brands of fruit were used by Zoller for oil analysis. They were thoroughly washed and all pulp removed. It was noticed that the distribution of the oil sacs in the pericarp varied considerably in the different varieties, some being especially rich in oil, others comparatively poor.

The cleaned peels were cut by a revolving food chopper into pieces averaging a centimeter in cross-section. Trial methods of isolating the oil were tried. A small hand-press cider extractor was employed, yielding a liquid emulsion of solids, oil and water. When this emulsion was allowed to stand for several hours there was a slight separation of the oil on the upper surface but it was always turbid and intensely bitter. Centrifuging and freezing were tried to free the oil from the accompanying material and while it was in a measure successful, this would be inadvisable on a large scale. Precipitation of the astringent material, pectose, and resins by means of gelatin and tannic acid solution gave a somewhat clearer oil, but its flavor was repugnant.

Extraction of the oil by means of volatile solvents gave a good yield of oil but was laborious, and in case of the solvents employed (acetone and ethyl alcohol) the bitter glucoside and resins were extracted at the same time.

The method finally adopted and which resulted in a clear, slightly yellow oil was as follows: The finely cut peel was introduced into a roomy con-



(Jour. Ind. and Eng. Chem.)

FIG. 9.—Apparatus for grapefruit oil extraction

tainer with an equal weight of water. Slight suction was applied by means of a water pump furnishing a steady reduction of pressure. Live steam was then drawn through the suspended peel and condensed in a suitable condensing apparatus connected with the suction (see *F* in Fig. 9). Steam distillation was continued until the condensate was free from turbidity, which point indicated that the oil was entirely removed. A second receiver was connected with the suction in series with *F*, and this second receiver was submerged in brine-ice mixture in order to entrap any of the oils which might tend to be drawn past *F*. Buffers of glass wool were placed in the second receiver as an additional precaution. A slight amount of oil was recovered this way. The oil separated on the surface after a few minutes' standing, and was drawn off. The remaining traces were removed from the distillate by centrifuging.

From 0.4 to 1.1 per cent of oil was obtained. A decrease in the aldehyde content of the oil during storage was manifested.

One hundred gm. of the steam-distilled oil, collected under diminished pressure as indicated above, was washed several times with 50-c.c. portions of normal Na_2CO_3 solution, then with water, and finally dried with anhydrous sodium sulphate. The physical properties of the oil in this condition were determined as stated above under properties.

One hundred gm. of the washed and dried oil was distilled from a flask fitted with a Hempel column under a constant pressure of 12 mm. The distilling flask was immersed in a bath of cottonseed oil and the temperature very gradually increased. The distillate was collected in the following fractions, the boiling-point of each fraction being determined and the approximate results given in Table V.

TABLE V

Fraction No.	Boiling Point Range	Weight (Grams)	Boiling Point
1	48– 52°	2.4	158°
2	52– 58°	71.5	172°
3	58– 70°	14.2	178°
4	70– 85°	1.3	181°
5	85–100°	4.8	200°*
6	100–115°	3.6	230°

*Rapidly rising to 225°, then dropping rapidly and browning. Fractions 2 and 3 were mixed together for qualitative analysis, also Nos. 5 and 6, since the range in either case is similar.

α-Pinene.—Fraction 1 and the mixtures of Fractions 2 and 3 were used. Pinene was tested for in these separate fractions by the nitrosyl chloride method described by Wallach and Ehestadt, and its presence in both mixtures established by the melting-point of the obtained pinene-nitrosochloride, 102° and 103°C. The largest yield was, of course, from Fraction 1. Crystals of pinene-hydrochloride were also prepared from Fraction 1 which melted at 132°C.

d-Limonene.—A portion of the mixture of Fractions 2 and 3 distilled under atmospheric pressure gave a distillate which was collected at the

approximate temperature of pure limonene, 175°C. The solution was strongly dextro-rotatory, +38 in a 100-mm. tube at 20°C. As further proof, 5 gm. of crystalline limonene-tetrabromide were prepared which melted at 104°C. Limonene was also detected in Fraction 4, though in small amount.

Aldehydes in limonene fraction.—10 gm. of the limonene fraction indicated only a possible trace of alcohols. Fraction 4 indicated at least 10 per cent of its weight as of alcohols, calculated as linalool $l(CH_3)_2C:CH\cdot CH_2CH_2C(OH)(CH_3)CH:CH_2$. The mixture of Fractions 5 and 6 indicated approximately 4 per cent of their combined weight, calculated as geraniol $l(CH_3)_2C:CH\cdot CH_2C(CH_3):CH\cdot CH_2\cdot OH$).

Linalool.—Fraction 4 consisting of a little over one gram was shaken in a small glass-stoppered flask with an excess of 5 per cent sulphuric acid. After a short time crystals of terpine hydrate ($C_{11}H_{20}O_2H_2O$) separated, which melted at 116°. The oxidation of linalool to citral was impossible to detect in this connection, since citral was also present, judging by the odor and by the test under aldehydes.

Citral.—While citral was known to be present both from the odor and from the boiling-point of the last two fractions, in the latter case suffering decomposition, it was further identified by its semicarbazide preparation. The semicarbazone, prepared according to Zelinsky, melted sharply at 165°.

Geraniol.—One gm. of Fraction 6, before mixing with 5, was shaken vigorously with 5 per cent aqueous H_2SO_4 and after standing for one hour the acid was neutralized with 10 per cent NaOH. Upon further standing crystals of terpine hydrate separated which melted at 116°C. It was assumed that none of the linalool appeared in Fraction 6, since its boiling-point is slightly below 200°C. at atmospheric pressure, while Fraction 6 boils under the same conditions at approximately 230°C.

The oil from grapefruit is apparently less perfectly known than any of the citrus oils, which may seem somewhat remarkable in view of the large and rapidly growing quantity of new material in the form of unsalable fruit available for its production. The explanation may well be that grapefruit as a commercial commodity obtained its popularity within a comparatively short time. Now that its production is growing at a pace which promises to exceed the present demand a consideration of possible by-products is becoming a matter of increasing importance, and this oil should have fuller investigation. There seems to be no reason why for certain purposes it should not be found equal to lemon and orange oil.

ESTERS IN ESSENTIAL OILS

Although the estimation of esters in essential oils is of extreme value, considerable difficulty in correctly interpretating results obtained has recently been introduced on account of the abuse of scientific knowledge which has led to the preparation of a series of artificial

esters, most of which have a saponification value which would indicate the presence of considerably more natural ester than the actual amount of artificial ester used as an adulterant. The principal esters used in connection with these frauds are as follows: Terpinyl acetate, glyceryl acetate, ethyl citrate, ethyl oxalate, ethyl succinate, ethyl tartrate, and ethyl phthalate. Apart from the actual identification of the acid constituents of these esters, the following notes in regard to one or two of them will be of value.

TERPINYL ACETATE

This ester is principally found as an adulterant in oil of bergamot, oil of petitgrain, and similar essential oils. The natural ester present in this class of oil consists principally of linalyl acetate. Linalyl acetate is hydrolyzed at a considerably more rapid rate than terpinyl acetate. It, therefore, becomes possible to state with certainty that an artificial ester, probably terpinyl acetate, is present in either of these oils when a marked difference is found between the saponification value as determined at thirty minutes, and that determined in sixty minutes. From Table VI[1] it will be seen that hydrolysis of linalyl acetate or of bergamot oil is practically complete in thirty minutes, whereas the saponification of terpinyl acetate or of bergamot oil adulterated with this ester is much slower.

TABLE VI

Ester	Time of Saponification (Minutes)					
	5	15	30	45	60	120
Linalyl acetate (Schimmel & Co.)	191.5	217.5	223.2	223.7	223.1	224.7
Terpinyl acetate	108.2	166.8	209.7	233.4	245.8	262.7
Bergamot oil	80.3	94.5	97.3	97.5	97.8	98.5
Bergamot oil + 5 per cent terpinyl acetate	82.5	94.8	101.2	102.1	104.7	107.2
Bergamot oil + 10 per cent terpinyl acetate	79.9	96.4	102.8	105.2	108.3	112.5
Bergamot oil + 25 per cent terpinyl acetate	78.8	100.6	108.2	116.4	119.0	126.8

Still greater are the differences when one operates with dilute solutions for the shorter saponification period and with a large excess of alkali for the longer period. After numerous experiments Schimmel & Co.[2] have prepared the following directions for this fractional saponification method:

Four separate experiments are made. About 2 c.cm. of oil are accurately weighed in each case, dissolved in about 5 c.cm. of alcohol and a few drops of alcoholic phenolphthalein solution (1 : 100) added. The acid value is first determined with N/2 potassium hydroxide. To each of two of the flasks 10 c.cm. of N/2 potassium hydroxide are added and the contents heated on the water bath for an hour in order to effect saponification

[1] *Report of Schimmel & Co.* (October, 1911), p. 116.
[2] *Report of Schimmel & Co.* (October, 1910), p. 60.

in the well-known manner. The contents of the third flask are boiled with 20 c.cm. of the alkali for two hours and that of the fourth flask diluted with 25 c.cm. neutral 96 per cent alcohol and saponified for one hour with 10 c.cm. of the standard alkali. For oils with a high percentage ester content 30 and 15 c.cm. respectively of the standard alkali are used, and in the case of artificial esters as much as 40 and 20 c.cm. respectively for the third and fourth flasks. At the close of the boiling, the flasks are quickly and uniformly cooled by placing them in cold water and the contents are titrated immediately.

In the case of bergamot and lavender oils the difference in the ester values, obtained by boiling for two hours and with the dilute solution for one hour, amounted to 3 or at most 4, whereas the ester values for the two normal determinations represented the approximate mean of these extremes. If terpinyl acetate be added, this difference increases. Moreover, the ester value obtained for the two-hour saponification increases in the ratio in which the terpinyl acetate is added, whereas that obtained for the oil diluted with alcohol increases but little. The ester values of the two normal saponifications invariably are intermediate. In Table VII the data have been compiled for a pure bergamot oil and also for the same oil to which terpinyl acetate had been added in the proportions indicated.

TABLE VII

Seminormal Potassium Hydroxide.....	10 c.cm.	20 c.cm.	10 c.cm. + 25 c.cm.alc.	Difference between Columns 2 and 3
Duration of Saponification.....	1 Hour	2 Hours	1 Hour	
Bergamot oil, pure.....	99.7	100.5	97.4	3.1
+ 2 per cent terpinyl acetate.....	102.1	104.5	98.1	6.4
+ 4 per cent terpinyl acetate.....	103.3	108.1	98.1	10.0
+ 6 per cent terpinyl acetate.....	105.7	112.2	98.6	13.6
+ 8 per cent terpinyl acetate.....	107.0	114.4	98.4	16.0
+10 per cent terpinyl acetate.....	108.6	118.1	99.1	19.0
+15 per cent terpinyl acetate.....	113.4	126.7	101.0	25.7
+20 per cent terpinyl acetate.....	118.0	135.6	101.3	34.3

Hence an addition of 10 per cent terpinyl acetate produces a difference of 19 in the ester values. (In the case of normal saponification for one-half and one hour duration respectively, the difference is but 5.5.) Inasmuch as the addition of but 2 per cent of ester produces a difference of 6.4, the presence of even small amounts of adulteration can possibly be detected in this manner.

CITRIC ACID ESTERS

If the residue of an oil is found too high, adulteration with fatty oil is no longer the only explanation, for in recent years citric acid triethyl ester (triethyl citrate [Wiegand and Rübke]) must likewise be considered. The latter is a particularly serious adulteration since the addition of but small amounts materially increases the apparent ester content of the oil.

If a given oil is suspicious because of its high evaporation residue, this is transferred quantitatively to a saponification flask with the aid of alcohol and saponified in the usual manner with N/2 potassium hydroxide. The excess of alkali is titrated back with N/2 sulphuric acid, phenolphthalein being used as indicator. The first decoloration of the indicator is taken to indicate the end of the reaction, for subsequent reappearances of the red color may be due to the liberation of alkali by transformation of bergaptenic acid into bergaptene. The reappearance of the red color can be avoided in part by not diluting the saponification liquid with water previous to the back titration.

The saponification value of the evaporation residue of pure bergamot oils lies between 136 and 200. The addition of 1 per cent triethyl citrate increases the saponification value of the evaporation residue by 47.7. If one considers that 1 gm. of triethyl citrate requires as much alkali for saponification as 2.13 gm. linalyl acetate, it becomes apparent that, e.g., 2 per cent of added citric acid ester will increase the apparent linalyl acetate content of the oil by 4.3 per cent, i.e., by an amount which under certain circumstances may suffice seemingly to bring an oil poor in ester up to the normal standard.

Noteworthy is the behavior of oils thus adulterated during saponification. Whereas pure bergamot oils yield clear solutions with alcoholic potassium hydroxide, those adulterated with citric acid ester are rendered turbid more particularly at the beginning of the saponification because of the formation of potassium citrate which is difficultly soluble in alcohol.

In order to prove the presence of citric acid as such, the calcium test may be applied. Two gm. of oil or the evaporation residue of 5 gm. of oil are saponified with alcoholic potassium hydroxide, the solution diluted with water, neutralized with hydrogen chloride, the alcohol evaporated from a water bath, the solution shaken out with ester and then filtered. The filtered solution is rendered slightly alkaline with sodium hydroxide, a few drops of concentrated calcium chloride solution are added and the mixture heated. The presence of citric acid is indicated by the formation of a precipitate, which, however, may require some time to form.

The following method of identifying citric acid is due to Denigès: 10 c.c. of the saponification liquor from which the separated oil had been removed are shaken with 1 gm. of lead peroxide, and 2 c.c. of solution of mercuric sulphate of about 5 per cent strength. After vigorous shaking the liquid is filtered and 5 c.c. of the filtrate heated to boiling-point, and a 2 per cent solution of potassium permanganate added drop by drop, constantly stirring until it ceases to become immediately decolorized. If citric acid is present a flocculent pale-yellow or white precipitate develops after the first drop.

This reaction is much more delicate than the calcium test. With some practice it is even possible to approximate the citric acid ester content of the oil to be examined by comparing the results with those obtained from oils of known citric ester content. Great care should, however, be exercised with the addition of the potassium permanganate, for otherwise manganese peroxide may be precipitated, which may be mistaken for the precipitate described above (double salt of mercury and acetone dicarboxylic acid).

When six samples of bergamot oil, guaranteed pure, were tested by Schimmel & Co.,[1] according to Denigès' method, two of these revealed traces of citric acid. This small amount may have been introduced from the pulp rich in citric acid during the process of expression. As a matter of fact the traces were so slight that they need not be taken into consideration in practice. If, however, but 1 per cent of triethyl citrate be added to such an oil, Denigès' test yields a precipitate ten times as voluminous. Moreover, the evaporation residue of these authentic oils revealed low saponification values; if the latter exceed 200, the oil may be regarded as suspicious.

GLYCERYL ACETATE

This adulterant is usually a mixture of glyceryl acetates in which triacetin predominates. Its detection is moderately easy on account of the fact that it is readily soluble in very dilute alcohol, and even fairly soluble in water. Schimmel & Co.[2] have proposed the following methods for its detection.

Ten c.c. of bergamot oil are mixed in a separating funnel with 10 c.c. of light petroleum and 2.5 c.c. of alcohol, and vigorously shaken up with 20 c.c. of water. The addition of light petroleum and alcohol causes a very rapid separation of the oil and the aqueous liquid, so that the latter can be filtered off when the mixture has been allowed to settle for about ten minutes. Of the filtrate, ten c.c. are neutralized with potassium hydroxide and saponified on the water bath for one hour with 5 c.c. N/2 potassium hydroxide solution. In the case of pure bergamot oil, the 10 c.c. of filtrate required for saponification: 0.08 c.c. N/2 potassium hydroxide solution, i.e., 2.2 mg. KOH. After adding 1 per cent of glyceryl triacetate 0.58 c.c. 16.2 mg. KOH were used. After adding 2½ per cent of glyceryl triacetate 1.43 c.c. 40.0 mg. KOH were used. After adding 5 per cent of glyceryl triacetate 2.79 c.c. 78.0 mg. KOH were used.

Hence the addition of 1 per cent triacetate requires about 15 mg. KOH more for saponification.

Later, Schimmel & Co. proposed omitting the petroleum ether and shaking up 10 c.c. of the oil with 20 c.c. of 5 per cent alcohol. After allowing the two layers to separate completely 10 c.c. of the aqueous layer, which may be filtered, is neutralized, using phenolphthalein as indicator, and saponified for one hour with 5 c.c. of N/2 potassium hydroxide solution. With pure oils not more than 0.1 c.c. of N/2 alkali should be required, a higher figure indicating the presence of glyceryl esters. The time taken for the separation of the oil and the aqueous liquids is so long, however, that the use of petroleum ether is preferable. For the positive identification of glyceryl acetate, the same chemists describe the following process.

Forty gm. were hydrolyzed with the calculated quantity of sodium hydroxide in a concentrated aqueous solution; the solution was then distilled, and, as only water passed over, it was next evaporated to dryness in a dish. The attempt to separate the alcohol (glycerol ?), which had been split off from the ester, from the sodium salt of the acid by means of an extracting agent failed, because the known solvents took up not only the

[1] *Report* (October, 1910), p. 63.

[2] *Half-Yearly Report* (October, 1910), p. 61); (April, 1911), p. 150.

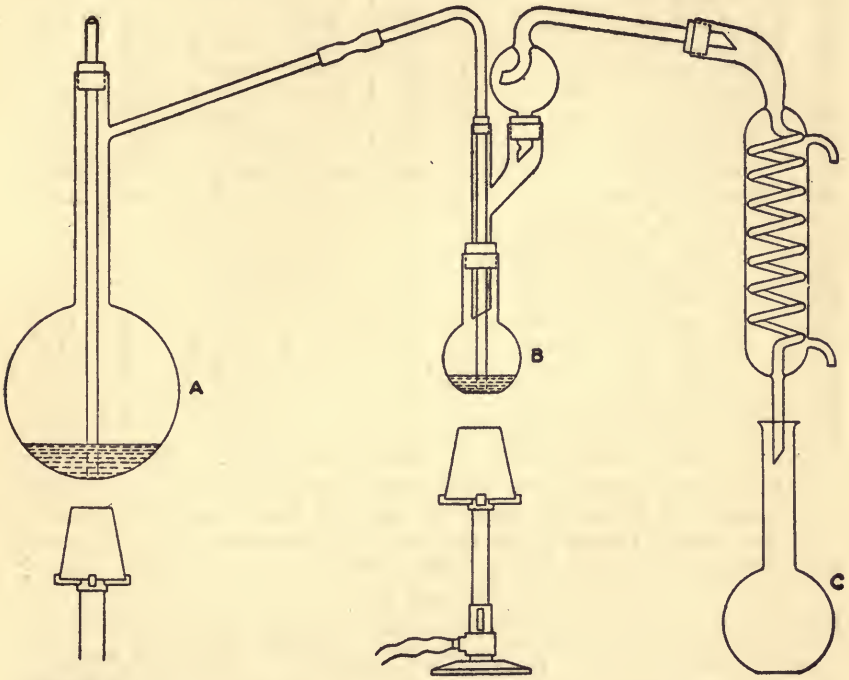
alcohol but also considerable quantities of the sodium salt. To obviate this difficulty the sodium salt was decomposed with the calculated quantity of dilute sulphuric acid and the organic acid which was liberated removed by distillation, and subsequently by evaporation. This acid was identified as acetic acid. It was now easy to separate the alcohol of the ester from the residual sodium sulphate by means of ethyl alcohol. When the ethyl alcohol had been evaporated by distilling *in vacuo,* the ester alcohol was identified as glycerol by its boiling-point 147° (4 mm.).

As Salamon and Seaber have pointed out, glyceryl acetate is so easily washed out with 5 per cent alcohol, that an adulterated oil, when washed several times with alcohol of this strength, will show a distinctly lower ester value than the original unwashed oil. Pure oils of lavender, bergamot, and similar oils show practically no reduction in ester value by such treatment.

NON-VOLATILE ESTERS

When non-volatile or practically non-volatile esters such as ethyl citrate are used for the purpose of adulteration, almost the whole of the esters remain in the residue left on evaporating the oil for from three to four hours on a water bath. If the weight of this residue is above the normal for a pure oil, non-volatile esters are strongly indicated and may be approximately determined by estimating the saponification value of the residue itself. The process is carried out as follows: Five gm. of the oil are evaporated in a platinum dish on a water bath until the weight is practically constant. The residue is washed into a flask and saponified in the usual manner. Titration should be effected quickly with phenolphthalein as indicator. After the neutral point has been reached, the liquid will acquire a red tint in a short time. No notice need be taken of this as it is due to decomposition of bergaptene or similar bodies. The saponification value of the residue from pure bergamot oil varies from about 135 to 180, usually about 170. The addition of 1 per cent of ethyl citrate will raise it about 50, while the addition of 2 per cent will raise it by nearly 100. Schimmel & Co. have devised the following method of estimating the amount of fixed esters present as an adulterant in this type of oil. The examination of pure bergamot oil has shown that almost the whole of the acid which is combined with the potassium hydroxide on saponification can be distilled off with steam after acidifying the aqueous solution with sulphuric acid. With pure bergamot oil, therefore, only a little more potassium hydroxide solution is used in ascertaining the saponification number than is required for neutralizing the acids which have been distilled off. The estimation is carried out with 1.5 to 2.0 gm. of the oil as follows: the acid and ester numbers are ascertained in the usual manner, and the contents of the saponification flask evaporated to dryness after adding a few drops of N/2 potassium hydroxide solution. The residue is dissolved in about 5 c.c. of water and acidified with 2 c.c. of dilute sulphuric acid. From the flask *A* (Fig. 10), fitted with an ascending tube, a powerful current of steam is generated, by which, in about half an hour, 250 c.c. is distilled over into the measuring flask *C* in such a manner that the contents of the saponification flask *B* are kept down to about 10 c.c. with a

small flame. Afterward 100 c.c. more are carried over in the same manner. The distillate, after a few drops of phenolphthalein solution have been added, is titrated with N/2 potassium hydroxide solution (or for the sake of accuracy, better still with N/10 solution) until it assumes a red color. The first 250 c.c. contain very nearly the entire volatile acids, as the next 100 c.c. invariably use up only 0.1 to 0.2 c.c. of N/2 solution. From the quantity of potassium hydroxide solution required to neutralize the entire distillate the acid number (II) is calculated for the weight of the bergamot



(Schimmel & Co.)

FIG. 10.—Apparatus for estimations of fixed esters

oil used. The difference between the saponification number of several pure oils which have been examined and the acid number (II) determined in the manner described above, varied (as shown in Table VIII, from Allen, Nos. 1-7) from 5.2 to 6.9.

Hence, unless further examination of pure oils should show a higher figure, oils with greater difference must be regarded as suspected or adulterated.

In the case of the pure esters (Nos. 12 to 14) here examined the difference between the two values was from 596.4 to 745.8. The addition of such esters to oil of bergamot must, therefore, correspondingly increase the difference of both numbers of the adulterated oil (Nos. 15 to 23 of the table).

TABLE VIII

	Acid No. of Oil	Ester No. of Oil	Sap. No. of Oil	Acid No. II of the Oil	Difference
No. 1 Bergamot oil	1.6	88.7	90.3	84.3	6.0
No. 2 Bergamot oil	1.6	90.2	91.8	86.6	5.2
No. 3 Bergamot oil	2.0	101.1	103.1	97.0	6.1
No. 4 Bergamot oil	2.3	112.3	114.6	107.7	6.9
No. 5 Bergamot oil	2.4	100.0	102.4	95.7	6.6
No. 6 Bergamot oil	2.3	96.1	98.4	91.8	6.6
No. 7 Bergamot oil	2.1	98.3	100.4	95.1	5.3
No. 8 Bergamot oil	2.0	98.2	100.2	90.8	9.4
No. 9 Bergamot oil	2.0	103.9	105.9	91.8	14.1
No. 10 Bergamot oil	2.0	102.4	104.4	87.6	16.8
No. 11 Bergamot oil	2.8	103.9	106.7	89.9	16.8
No. 12 Diethyl succinate	...	.....	638.4	7.3	631.1
No. 13 Triethyl citrate	0.8	602.6	603.4	7.0	596.4
No. 14 Diethyl oxalate	...	.....	753.0	7.2	745.8
Bergamot oil after adding:					
No. 15 1 per cent Diethyl succinate	2.1	103.5	105.6	94.1	11.5
No. 16 2 per cent Diethyl succinate	2.1	109.9	112.0	93.1	18.9
No. 17 3 per cent Diethyl succinate	2.1	116.2	118.3	92.8	25.5
No. 18 4 per cent Diethyl succinate	2.1	121.7	123.8	91.8	32.0
No. 19 5 per cent Diethyl succinate	2.1	127.6	129.7	91.5	38.2
No. 20 1 per cent Triethyl citrate	2.1	103.4	105.5	94.1	11.4
No. 21 2 per cent Triethyl citrate	2.1	109.1	111.2	92.8	18.4
No. 22 1 per cent Diethyl oxalate	...	.....	106.6	94.7	11.9
No. 23 2 per cent Diethyl oxalate	...	.....	113.3	92.5	20.8
No. 24 2 per cent Glyceryl triacetate	2.1	111.2	113.3	108.7	4.6
No. 25 4 per cent Terpinyl acetate	2.4	103.2	105.6	100.0	5.6

Nos. 24 and 25 show that adulteration with the esters of the volatile group cannot be detected by distilling the acids, because in these cases the difference lies of course within the limits for pure oils. Table IX shows average figures for a number of artificial esters.

TABLE IX

Ester	Specific Gravity 15°C.	Refractive Index 20°C.	Ester (Per Cent)	Range of Boiling-Point
Ethyl formate, pure	0.908	1.3621	74.9	54°- 65°
Ethyl formate, commercial	0.869–0.927	1.360–1.367	59.6- 68.9	55°- 80°
Ethyl acetate, pure	0.904	1.3740	100.8	75°- 79°
Ethyl acetate, commercial	0.901–0.904	1.3737–1.374	82.8- 94.7	71°- 84°
Ethyl butyrate, pure	0.883	1.3922	100.1	110°–120°
Ethyl butyrate, commercial	0.883–0.886	1.388–1.492	95.4–100.5	105°–149°
Ethyl succinate	1.042–1.054	1.419–1.421	98.0- 99.5	210°–214°
Ethyl sebacate	0.959–0.966	1.436–1.439	94.9- 96.4	Above 300°
Ethyl benzoate	1.048–1.053	1.504–1.545	73.8–100.5	210°–215°
Ethyl cinnamate	1.053–1.056	1.557–1.559	99.1–100.6	260°–267°
Ethyl salicylate	1.132–1.134	1.521–1.523	96.0- 99.8	225°–230°
Amyl acetate, pure	0.860–0.863	1.397–1.402	89.6- 99.6	130°–140°
Amyl acetate, commercial	0.864–0.870	1.399–1.402	82.2- 88.9	110°–142°
Amyl butyrate, pure	0.867	1.4128	99.9	170°–180°
Amyl butyrate, commercial	0.857–0.867	1.407–1.412	76.9- 83.4	135°–180°
Amyl valerate, pure	0.858	1.4131	98.7	180°–190°
Amyl valerate, commercial	0.850–0.866	1.408–1.413	75.6- 81.8	140°–190°
Amyl salicylate	1.048–1.053	1.505–1.508	97.2- 98.7	260°–275°

METHODS OF CITRAL ASSAY

1. The first attempt to determine quantitatively the amount of citral in lemon oil was made by H. Garnett, who reduced the aldehydes to alcohols by means of sodium and attempted to assay the latter by acetylation. As detailed experiments have revealed, the reaction is unfortunately not quantitative, hence the results are useless.[1]

2. *Method of J. Walther.*—Walther has utilized citraloxime for the quantitative determination of this aldehyde. An alcoholic solution of hydroxylamine hydrochloride of known strength is boiled with a definite amount of lemon oil (about 10 gm.) and some sodium bicarbonate for three-fourths of an hour on a water bath in a long-necked flask connected with a reflux condenser. After cooling, the amount of unconsumed hydroxylamine hydrochloride in the reaction mixture is determined titrimetrically with N/10 sodium hydroxide solution. The difference between the amount of hydroxylamine hydrochloride originally employed and that thus found represents the amount that has entered into reaction with the citral and admits of the computation of the latter. On account of the inaccurate results the method has not been followed.[2] For this reason it has been modified by A. H. Bennett.[3] In order to avoid the evolution of carbon dioxide, and with it the occasional loss of hydroxylamine, he has employed caustic potash in place of sodium bicarbonate. The amount of alkali is chosen so that an excess of hydroxylamine with reference to the citral is liberated from its hydrochloride, but that some of the hydrochloride remains unchanged. To a mixture of 20 c.c. of lemon oil and 20 c.c. N/2 alcoholic (80 per cent) hydroxylamine hydrochloride solution, 8 c.c. alcoholic normal potassium hydroxide solution and 20 c.c. of aldehyde-free strong alcohol are added and the mixture boiled for one-half hour in a flask connected with a reflux condenser. After the reaction mixture has cooled, 250 c.c. of water are added, part of which is used to rinse the reflux condenser, and the hydrogen chloride still combined with the hydroxylamine is neutralized, phenolphthalein being used as indicator. The hydroxylamine not combined with the citral is then titrated with N/2 sulphuric acid, the end reaction being ascertained by removing drops to be tested with methyl orange as indicator. A blank is conducted in like manner but without lemon oil in order to ascertain the factor of the hydroxylamine solution. From the difference in the half-normal sulphuric acid consumed in the two experiments the amount of hydroxylamine that has entered into reaction can be ascertained and the amount of citral can be computed by multiplication with 0.076. The serviceability of the method was determined by Bennett by using pure citral. When lemon oil was tested the citral content fluctuated between 4.3 and 5.2 per cent.

Schimmel & Co.[4] found that by adding pure citral to the oil the results were too low by 10 per cent.

[1] *Report of Schimmel & Co.* (October, 1896), p. 41.

[2] *Report of Schimmel & Co.* (April, 1900), p. 22; *ibid.* (October, 1901), p. 26.

[3] From a lengthy experience in these processes, E. J. Parry has no hesitation in saying that the most accurate method for the estimation of citral in lemon oil is this modification suggested by Bennett.

[4] *Report of Schimmel & Co.* (October, 1909), p. 153.

3. *Method of A. Soldaini and E. Bertè.*—Five c.c. of lemon oil are measured at a definite temperature in a cylindrical pipette graduated into 1/40 c.c. and allowed to flow into a 100 c.c. fractionating flask, the neck of which is so contracted that it can be connected with the inverted pipette by means of a rubber tube. The lateral tube of the fractionating flask is bent upward and can be closed by means of a piece of rubber tubing and pinch cock. To the oil in the fractionating flask 25 c.c. of a saturated solution of potassium acid sulphite solution, containing some free acid, are added and the mixture shaken thoroughly. The mixture is then digested for ten minutes in a boiling water bath, care being taken to shake the flask at short intervals and to see to it that it does not become hotter than is convenient to the touch if the bulb is held in the hand. The contents are then allowed to cool with constant shaking, again heated for five minutes and finally allowed to cool completely without interruption in the shaking. The lateral tube is now connected with a funnel, through which water can be added as desired to the flask, and the inverted cleansed and dried pipette is connected by means of a rubber tube with the upper, contracted end of the fractionating flask. Water is now added through the funnel and, assisted by rotation and tapping, the floating oil is induced to rise into the pipette. For the purpose of removing any oily particles that adhere to the neck, air is forced through the lateral tube. The air will carry with it any oil. After all of the oil has thus been collected in the pipette, it is allowed to become clear by standing and its volume read off and the difference computed as volume of citral. For the determination of the approximate percentage by weight an average specific gravity of 0.859 is taken.

This method has proved inexpedient because at the border of the oily and aqueous zones a mucilaginous and salty layer is formed which renders an exact reading impossible.

4. *Method of E. J. Parry.*[1]—Parry has suggested to determine the citral content of lemon oil with the aid of citrylidene cyanacetic acid discovered by Tiemann. From 200 c.c. of lemon oil, about 175 c.c. are removed by fractional distillation under diminished pressure. The residue is measured and the temperature noted. To 10 c.c. thereof contained in a cassia flask a solution of 5 gm. of cyanacetic acid in 30 gm. of 15 per cent sodium hydroxide solution are added and the mixture shaken at a low temperature. The aldehyde of the oil dissolves in the aqueous-alkaline liquid, whereas the non-aldehyde constituents float on the solution. The volume of the latter is read off in the graduated neck of the flask at the same temperature at which the volume of the residue of the oil was determined. The number of c.c. read off is deducted from 10. This difference with reference to the original volume of oil used (200 c.c.) computed for 100 parts of lemon oil reveals the percentage content of aldehyde.

Although the results obtained with citral mixtures of known content agreed fairly well (as a rule they were somewhat too high), the method is not applicable to lemon oil, since an accurate reading is rendered impossible

[1]This process according to Parry does not give satisfactory results, and is only quoted here as Parry definitely withdraws it as a process associated with his name.

because of the separation of a mucilaginous layer at the zone of contact as is the case with the bisulphite method.[1]

5. *Method of S. S. Sadtler.*—This is based on Tiemann's observation that when citral is shaken with neutral sodium sulphite solution citral dihydrodisulphonic acid results, sodium hydroxide being formed at the same time:

$$C_9H_{15}CHO + 2Na_2SO_3 + 2H_2O = C_9H_{17}(SO_3Na)_2CHO + 2NaOH$$

By titration with semi-normal hydrogen chloride the amount of liberated sodium hydroxide is determined and from this the amount of citral computed. The method is carried out in the following manner:

Having neutralized the free acid in 5 to 10 gm. of lemon oil, contained in an Erlenmeyer flask, with semi-normal potassium hydroxide solution, five times the amount of a 20 per cent sodium sulphite solution are added, the sulphite solution having previously been neutralized with semi-normal hydrogen chloride at water bath temperature, rosalic acid being used as indicator. The mixture being shaken repeatedly is heated in a boiling water bath and the resulting sodium hydroxide neutralized from time to time. The reaction is completed as soon as the solution remains neutral, which occurs after about one-half hour. The amount of hydrogen chloride consumed is equivalent to the amount of liberated sodium hydroxide and this to the citral content of the oil. The following formula may be used in which a represents the number of c.c. of N/2 acid and s the amount of oil used.

$$\frac{3.8 \cdot a}{s}$$

The end reaction, however, is so indistinct that concordant results are not obtained. In the process of neutralizing the liberated sodium hydroxide with the acid, the original red color produced by the rosalic acid gradually passes over into pink, hence it is difficult to decide which shade of color is to be regarded as indicating the end of the reaction. Neither will it do to titrate the solution until an absolute change in color takes place, for then the results obtained are several per cent too high.[2]

6. *Method of G. Romeo.*—This method is very similar to Sadtler's and suffers from the same defect, viz., that the end reaction cannot be determined accurately. In trying out the method it was not even possible to standardize the solution accurately according to directions.[3]

This method is based on the reaction of citral with a solution of neutral and acid sulphite with the formation of a trihydrotrisulphonic acid according to the following equations:

1. $$C_9H_{15} \cdot C\begin{matrix}H\\O\end{matrix} + \begin{matrix}2Na_2SO_3\\NaHSO_3\end{matrix} + 2H_2O = C_9H_{17} \cdot (SO_3Na)_2 \cdot CH(OH)SO_3Na + NaOH.$$

2. $$2NaOH + 2NaHSO_3 = 2H_2O + 2Na_2SO_3.$$

[1] *Report of Schimmel & Co.* (October, 1900), p. 24.
[2] *Report of Schimmel & Co.* (April, 1914), p. 48.
[3] *Report of Schimmel & Co.* (October, 1905), p. 30.

According to the foregoing equations three acid equivalents correspond to one molecule of citral. For the assay a solution of 400 gm. $Na_2SO_3 + 7H_2O$ in 1 liter of water + 160 c.c. of a concentrated potassium acid sulphite solution are standardized against N/2 potassium hydroxide. Twenty-five c.c. of this are gently heated with 5 c.c. of lemon oil, titrated with acid, rosalic acid being used as indicator, and the citral content computed. Experiments were made with pure citral, solutions of citral in xylene of known aldehyde content, and citral-containing oils (ordinary as well as terpene-free). The results obtained by the author agree very well. Four lemon oils revealed a citral content varying between 3.64 and 4.48 per cent.

R. O. Brooks employs a neutralized potassium bisulphite solution in place of that of sodium sulphite. However, according to Schimmel & Co.,[1] this modification does not remove the defects of the method.

7. *Method of P. B. Rother.*—This method for the assay of aldehydes and ketones is based on their conversion into phenylhydrazones, the reaction of the excess of phenylhydrazine with iodine, and finally the titration of the excess of iodine with thiosulphate. According to E. Fischer the reaction between iodine and phenylhydrazine is expressed by the following equation:

$$2C_6H_5NHNH_2 + 2I_2 = C_6H_5N_3 + C_6H_5NH_2 \cdot HI + 3HI.$$

However, according to E. von Meyer, the reaction is modified by an excess of iodine as expressed by the following equation:

$$C_6H_5NH \cdot NH_2 + 2I_2 = C_6H_5I + N_2 + 3HI.$$

Fully 5 gm. of phenylhydrazine are dissolved in about 250 c.c. of warm water, the solution filtered to remove products into a half-liter flask. After cooling the flask is filled to the neck with boiled distilled water. The rather unstable solution is to be kept well stoppered and away from light.

The strength of the phenylhydrazine solution is determined in the following manner: 300 c.c. of water and exactly 40 c.c. of N/10 iodine solution are transferred to a liter flask. With the aid of a pipette, 10 c.c. of the phenylhydrazine solution are transferred to a small flask containing 50 c.c. of water and the diluted solution transferred to the liter flask. After about 1 minute the excess of iodine is titrated with N/10. thiosulphate. 0.1 gm. of pure phenylhydrazine corresponds to 37 c.c. of N/10 iodine solution.

Of the lemon oil to be examined, about 10 gm. are weighed in a weighing flask and in order to avoid oxidation several c.c. of alcohol are immediately added. With the aid of about 30 c.c. of alcohol the oil is then transferred to a flask of 250 c.c. Enough standardized phenylhydrazine solution is then added so as to supply one molecule of phenylhydrazine for every molecule of aldehyde or ketone. The mixture is then thoroughly shaken and set aside for about twenty hours protected against light and repeatedly shaken during this time. After this the unchanged oil is removed by means of a separating funnel and repeatedly washed with water, the washings being added to the liquid to be titrated. This liquid is still further

[1] *Report of Schimmel & Co.* (October, 1908), p. 156.

diluted with water and filtered through a pleated filter (if necessary with some gypsum), into a liter flask containing about 500 c.c. of water and 10 to 20 c.c. of N/10 iodine solution, the latter amount varying according to the amount of phenylhydrazine used. During the process of filtration the flask is shaken repeatedly. The filter having been carefully washed wtih water, the liquid is titrated with N/10 thiosulphate solution, starch solution being used as indicator.

The percentage of aldehyde being indicated by x, this can be computed with the aid of the following formula:

$$x = \frac{d \cdot M}{100 \cdot 4 \cdot s},$$

in which d is the difference between the amount of c.c. of N/10 iodine solution corresponding to the phenylhydrazine used and the actual number of N/10 iodine solution consumed, M the molecular weight, and s the amount of material used expressed in grams.

Upon trying out this method[1] it was found that, in general, useful results are obtainable but that these do not exceed in accuracy those obtained by the volumetric bisulphite method and the sulphite method. In daily practice it offers no advantage over the other two methods, both because of the instability of the required solutions and because it takes too long to ascertain the results. Neither is the method sufficiently reliable so that conclusions as to the quality of the oil can be drawn directly from the determined citral content. Indeed, the variations in the results are sufficiently large to admit of the passage of adulterated oils as good ones.

8. *Method of P. Bruylants.*—For a long time the blood spectrum has been employed for the detection of such substances as oxygen, carbon monoxide, and hydrogen cyanide by observing the change in the spectra produced by them. Recently Bruylants proceeding from the following considerations has utilized the spectroscopic behavior of the blood for the quantitative determination of aldehydes. If yellow ammonium sulphide and a small amount of aldehyde are added to defibrinated blood, the two absorption bands of the oxyhaemaglobin lose their intensity. Gradually a third band appears between them which increases in distinctness and ultimately acquires the same degree of intensity as the two bands of the oxyhaemaglobin. These are then modified still more. Bruylants points out that, according to his method, not only the citral but all of the aldehydes are determined in the lemon oil. So far as practical results are concerned this is of little consequence since the other aldehydes are present in small amount only as compared with citral.

For carrying out the determination the following instruments and reagents are needed: (1) A spectrophotometer after d'Arsonval the two fields of vision of which are arranged one above the other so as to admit of direct comparisons; also the containers for solutions belonging thereto, burettes and test tubes. (2) A 3 per cent blood solution, made from fresh, defibrinated pig's blood, which in the spectroscope shows the two bands characteristic of oxyhaemaglobin. (3) A solution of ammonium sulphide

[1] *Report of Schimmel & Co.* (October, 1907), p. 121.

which must be prepared with special care in order to obtain the desired results. (A definite volume of ammonia is saturated with hydrogen sulphide, a somewhat larger volume of ammonia is added, and the ammoniacal sulphide solution thus obtained exposed to the light for several days.) (4) Citral solutions of 3, 4, and 5 per cent citral in citral-free oil for comparison. (5) Aldehyde-free, 94 per cent alcohol prepared by boiling over potassium hydroxide and *m*-phenylenediamine hydrochloride.

Preliminary tests are made, preferably by two persons, to ascertain the approximate percentage of aldehyde. To 9 c.c. each of the blood solution, 1 c.c. of the ammonium sulphide solution is added, and then the solution of the oil to be examined to the one and the 5 per cent citral control solution to the other. The solutions should be prepared under exactly the same conditions. Both of the oil solutions are so prepared that for every c.c. of aldehyde-containing oil 5 c.c. of alcohol are used. At first 0.15 c.c. of each solution is added and the containers shaken for about one-half minute. After separation of the insoluble portions, the lower layer is removed by means of a pipette and transferred to the spectroscope tubes. When working fairly rapidly the oxyhaemaglobin bands can be located in both fields of vision. Then the band in the middle appears as first phase of the reaction. If the aldehyde content is the same in both solutions this middle band appears in both fields at the same time. If this is not the case the amount of the alcoholic solution of the oil is increased or diminished by one-hundredth part of a c.c., whereas the amount of the control solution remains the same. Thus, after five or six tests the aldehyde content can be ascertained approximately. In the subsequent exact determination, a control solution is used, the aldehyde content of which approximates that of the oil to be examined. If the oil contains less than 5 per cent aldehyde, a 3 or 4 per cent citral solution is used; if more than 5 per cent, the 5 per cent solution is employed and the solutions are tested until the middle absorption band appears at the same time. After some practice, a complete determination can really be made within a half-hour. The results are fairly exact. In an artificial oil with 5.06 per cent of citral, 4.9 per cent were found.

Several lemon oils were examined by Bruylants and the following volume percentage of citral ascertained:

Messina oil, 1906 harvest: 4.58 and 4.65 per cent; harvest of January, 1905: 5.42 and 5.52 per cent; harvest of November, 1904: 6.47 per cent.

Reggio oil, 1906 harvest: 5.10 and 5.14 per cent.

Two commercial oils contained 3.5 and 3.7 per cent, a third contained but 2.86 per cent citral.

Whatever the scientific interest may be that is attached to this method, from the point of view of the analytical laboratory it is much too complicated to be used in the assay of volatile oils. For this reason it apparently has not been used in practice.

9. *Method of E. M. Chace.*—This method is based on the property of fuchsinsulphurous acid to become red in the presence of aldehydes, the intensity of the red color depending on the amount of aldehyde present. A comparison with the color of solutions of known aldehyde content enables the determination of the aldehyde in the oil to be examined.

The following reagents are required: (1) Fuchsinsulphurous acid: 0.5 gm. fuchsin are dissolved in 100 c.c. of water and a solution containing 16 gm. of sulphurous acid is added. When decoloration has taken place, the solution is diluted to 1 liter. This solution has to be prepared fresh every two or three days since it spoils readily. (2) Alcohol of 95 per cent by volume that is absolutely free from aldehydes. In order to remove all but traces of the aldehyde, the alcohol is allowed to stand over alkali. The alcohol is then distilled and the distillate boiled for several hours with *m*-phenylenediamine hydrochloride, using 25 gm. per liter. After a second distillation the alcohol is ready for use. (3) A standard citral solution, i.e., a solution of 0.1 per cent of citral in 50 per cent aldehyde-free alcohol. These, as well as the following solutions, are prepared at a temperature of 15°. At this temperature all of the determinations are made, the several containers being kept at this temperature in a water bath for ten minutes before being used. Above all, a higher temperature is to be avoided.

The assay is carried out in the following manner: 2 gm. each of the oils to be examined are diluted to 100 c.c. with aldehyde-free alcohol. Four c.c. each of these solutions are transferred to flasks of the same size, 20 c.c. aldehyde-free alcohol added and then 20 c.c. of fuchsinsulphurous acid and the solution diluted to 50 c.c. with alcohol and well mixed. With the standard citral solution, like solutions are made for comparison. All solutions are allowed to remain in the water bath for 10 minutes when the intensity of the colors are compared either directly or with the aid of a colorimeter.

As tried out by Chace, this method yields fairly satisfactory results with mixtures of citral and limonene, the values found differing not more than 0.2 per cent on the average from the real citral content. With lemon oils the results were not as favorable, though here also the errors remained within 0.5 per cent.

While trying out this method, Schimmel & Co.[1] did not use the colorimeter, but compared the intensity of color directly. They prepared eight different mixtures of the standard citral solution with the fuchsinsulphurous acid and alcohol in such a manner that each subsequent mixture contained 1 c.c. solution = 1 mg. citral more than the preceding one: the first mixture containing 1 c.c. of standard solution = 1 mg. citral, the eighth one 8 c.c. of solution = 8 mg. citral. Thus it became apparent that up to 5 mg. citral content the mixtures revealed differences in color, whereas beyond 5 mg. the color became so intense that differences were no longer observable. Smaller differences than 1 mg. in the citral content of the solutions were directly observable, i.e., without colorimeter, only in very dilute solutions, i.e., up to about 2 mg. citral.

According to Schimmel & Co. the citral content of lemon oils cannot be determined with certainty in this manner, since the waxy constituents of the oil prevent the recognition of the tone of color with any distinctness. This results in appreciable errors. The amount of citral found by the comparison of colors is to be multiplied by 1250 to yield the citral content of the oil. If there is any doubt as to whether the color indicated a citral content of 3 mg. or 4 mg. (lesser differences cannot be determined for

[1] *Report of Schimmel & Co.* (April, 1907), p. 167.

lemon oil) the following percentages result: 0.003×1250=3.75 or 0.004×1250 = 5.0, hence results that differ by 1.25 per cent. For the low citral content of lemon oils this difference is too great for the oils themselves, though, no doubt, the method is applicable to lemon extracts. Indeed, Chace himself has expressed this view in his publication.

10. *Method of R. S. Hiltner.*—For the determination of citral in lemon extracts and oils Hiltner likewise recommends a colorimetric method. It is based on the observation that at room temperature the addition of citral to a dilute alcoholic solution of *m*-phenylenediamine hydrochloride causes the formation of a yellow color, the intensity of which increases with the citral content. For this purpose a 1 per cent freshly prepared solution of *m*-phenylenediamine hydrochloride in 50 per cent alcohol is employed. It must be perfectly colorless and clear, conditions that are attained, if necessary, by treatment and filtration with animal charcoal. By comparison with a solution of known citral content (0.25 gm. citral to 250 c.c. of 50 per cent alcohol), the citral content of an extract or oil can be determined.

For a determination 1.5 to 2.0 gm. of lemon oil are diluted with 90 to 95 per cent alcohol to make a 50 per cent solution. Of this solution 2 c.c. are transferred to the colorimeter tube, 10 c.c. of the phenylenediamine solution are added, and the mixture diluted to a definite volume. With the standard citral solution comparative mixtures are prepared until the same intensity of color has been produced as has resulted in the solution of the oil to be tested. From this the citral content of the oil can be computed.

If, according to directions, the tests are made at room temperature the reaction is influenced neither by the acetaldehyde of the alcohol, nor by the other constituents of the oil. However, for oils that have been altered by oxidation, the method cannot be used, for such oils, according to the degree of oxidation, produce a yellowish-green to greenish-blue color.

11. *Method of C. Kleber.*—Even before its publication this method had been used for a longer period by Schimmel & Co.[1] who tested it as to its utility. It was thus demonstrated that it is superior to all methods published hitherto, not only because it yields more reliable results, but also because it can be carried out more readily. It is based on the observation that phenylhydrazine can be titrated accurately with mineral acids when ethylorange is used as indicator and that the hydrazones which the phenylhydrazine forms with aldehydes and ketones react neutral toward ethylorange. Inasmuch as the phenylhydrazine solution decomposes very rapidly, it is best prepared fresh for each assay. At least no solution should be employed that is more than one day old. If necessary the phenylhydrazine is previously distilled in vacuum.

According to the directions, slightly modified by Schimmel & Co., about 2 gm. of oil are mixed with a freshly prepared 2 per cent alcoholic phenylhydrazine solution in a 50 c.c. glass-stoppered flask and set aside for one hour. Then 20 c.c. of N/10 hydrogen chloride are added and the liquids mixed by gentle shaking. Ten c.c. of benzene are then added and after the mixture has been shaken thoroughly it is transferred to a separating funnel. After having been allowed to stand for a short time, the 30 c.c. of acid layer are drawn off and filtered through a small filter.

[1] *Report of Schimmel & Co.* (April, 1912), p. 75.

Twenty c.c. of this filtrate to which ten drops of ethylorange solution (1:2000) have been added, are titrated with N/10 potassium hydroxide until a distinct yellow color appears. From this the amount of N/10 potassium hydroxide required for 30 c.c. of filtrate is computed. For the standardization of the phenylhydrazine solution a blank experiment, i.e., without oil is made. If the 30 c.c. of filtrate of the first experiment demands *a* c.c. of N/10 potassium hydroxide and *b* c.c. in the latter experiment, the citral equivalent of the amount of oil (*s* grams) use is *a*—*b* c.c. N/10 potassium hydroxide. Inasmuch as 1 c.c. of N/10 potassium hydroxide corresponds to 0.0152 gm. of citral, the percentage content of the oil can be computed with the aid of the following formula

$$\frac{(a-b)\cdot 1.52}{s}$$

The object of shaking out with benzene is to render clear the solution which has become turbid upon addition of the hydrogen chloride. This facilitates the recognition of the change in color.

In Table X are recorded the results obtained by this method with mixtures of known citral content. These clearly reveal the usefulness of the method.

TABLE X

CITRAL CONTENT OF THE SOLUTION (IN PER CENT)

Given.....	2	4	6	7.3
Found.....	2.4	4.1	6.2	6.9
	2.0	4.0	5.9	7.0
	.....	3.9	6.0	7.1

A comparison of the results obtained according to the several methods for the assay of citral reveals appreciable differences. Hence it is always necessary to report the method with the results. The citral content of pure or supposedly pure oils is recorded by the following investigators: Soldaini and Bertè: 6.5 c.c. in 100 c.c. oil; Parry (1900): 5 to 6 per cent; Parry (1903): 3 per cent; Sadtler: 5.26 per cent; Bertè: 6.85 to 7.4 per cent; Romeo: 3.64 to 4.48 per cent; Rother: 5.25 to 5.9 per cent; Bruylants: 2.86 to 6.47 per cent; A. H. Bennett: 4.3 to 5.2 per cent; Chace: 4.1 to 7.0 per cent.

Determined according to Kleber's method, which is pronounced the most reliable by several American chemists,[1] the citral content of pure lemon oils varies between 3.5 and 5 per cent and is mostly about 4 per cent.[2] Hence the citral content in different oils fluctuates by more than 70 per cent. For this reason the citral content admits of the detection of adulteration only then when this is considerable. Thus to an oil which originally contained 5 per cent of citral, 20 per cent of non-aldehyde constituents might be added without detection by this means. Nevertheless, the citral assay is indispensable in the valuation of a lemon oil.

[1]E. M. Chace, *Bureau of Chemistry, United States Department of Agriculture Bulletin No. 137* (July 20, 1911), p. 64.

[2]*Report of Schimmel & Co.* (April, 1914), p. 58.

TERPENELESS ESSENTIAL OILS

By subjecting the essential oils to careful distillation under reduced pressure, there are obtained as distinct fractions, the hydrocarbons or terpenes of the oils, and an odorous oxygenated portion, which can be kept behind in the distillation apparatus. The terpene fraction has comparatively little or no odor in most cases; while, as a rule the oxygenated or high-boiling fraction retains all the good qualities of the original oil in a heightened degree. In other words, the oil has been concentrated, and the residual valuable fraction is found to have a far greater solubility coefficient (in alcohol) than the original oil, a fact which is of considerable commercial importance. In certain cases, distillation, at however low a pressure, would cause decomposition of the valuable oxygenated constituents of the oil. When this is the case, the terpeneless oil is of very little value since it does not represent the unaltered concentrated oil. Some few oils contain so little terpene that the terpeneless oil possesses little advantage over the neutral product.

The chief constituents of essential oils, prepared in a pure state (e.g., citral, eugenol, safrol, etc.) have occasionally been termed terpeneless oils, but this is manifestly a misnomer. In many cases these products are inferior to the real terpeneless oils. The two classes should, however, be carefully differentiated and the term "terpeneless oil" restricted to the product properly coming under that description.

Völckel and Schweitzer in 1840 and Haensel in 1876 first pointed out the value of this procedure. Many other observers followed up their researches and the increased usefulness of the terpeneless products has been widely recognized. The terpenes as a class readily oxidize and resinify on exposure to air, and at the same time develop an unpleasant odor and taste. Essential oils, which are thus liable to lose their delicate odor and flavor on keeping, may therefore frequently be stored in a terpeneless state for a long time without deterioration. Thus the terpeneless oils are specially valuable in the manufacture of perfumes, liquors, and essences, and for medicinal purposes.

Table XI shows the physical characters of many of the best-known terpeneless oils. The data are chiefly due to Parry, though some are taken from Haensel's reports (H). With the exception of the first sample of bergamot oil all the samples were genuine terpeneless products.

The "concentrated oil of lemon" on the market contains about 10 per cent of terpenes and is therefore to be distinguished from the terpeneless oil. True terpeneless oil of lemon is freed from the greater portion of the natural stearopotone by allowing the latter to separate after the distillation of the terpenes; or the oil is prepared by distilling 90 per cent of natural oil of lemons under reduced pressure, and steam-distilling the residue, when the terpeneless oil comes over practically free from citraptene. The yield

of terpeneless oil is from 5 to 6 per cent, containing approximately half its weight of citral.

TABLE XI

SPECIAL CHARACTERS OF ESSENTIAL OILS

Terpeneless Oil	Sp. gr. at 15.5°	Angle of Rotation (Degrees)	Vols. of Alcohol Required for Complete Solution
Bergamot*	0.903	−1.25	
Bergamot	0.8855	−9.25	8 of 60 per cent (H)
Bergamot	0.885	−7.9	
Lemon†	0.896 to 0.900	−7 to 9	5–20 of 70 per cent; 260 of 60 per cent contains 42–67 of aldehydes.
Limes (exprd.)	0.896	−8.6	
Limes (distilled)	0.92	−2.2	
Orange	0.894	+5 to +10	2 of 70 per cent (H).

*Probably contained artificial linalyl acetate (Parry).

†Burgess and Child have recorded a number of figures showing the composition and behavior on fractionation of terpeneless oils of lemon (*Journal of the Society of Chemical Industrial*, XX [1901], 1176).

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CHAPTER III

PRODUCTS FROM THE RIND—PECTIN[1]

Pectin, also called parapectin, is produced naturally in the ripening of fruit. It forms a colloidal solution in water and is the gelatinizing substance in fruit jellies. In the unripe fruit it is represented by its mother-substance protopectin, while in over-ripe fruit it becomes pectic acid. It may be produced by various chemical means from protopectin. It is present in large quantities in oranges, lemons, and grapefruit.

When pure it is white, odorless, and tasteless with practically the same gelatinizing properties as gelatin. Its usefulness depends on the fact that it may be employed in combination with various fruits that contain little or no pectin, such as strawberries, cherries, and peaches, to form jellies with the respective character and flavor of the latter.

For various purposes pectin is superior to gelatin. It lacks the odor of the animal product, is not a vehicle for tetanic infection or of impurities such as zinc and arsenic occasionally present in small quantities in gelatin.

SUMMARY OF EXPERIMENTAL PROGRESS

This "plant gelatin" was discovered by Braconnot in 1833. Nearly a hundred years have passed since then, yet its chemical constitution is still the subject of investigations and arguments.

Perhaps the most important of the old experiments on pectin are those of Frémy. According to him the pectin in unripe fruit occurs chiefly in an insoluble form as pectose. This body has never been isolated in a pure state as it has never been separated by any solvent from its accompanying substances, e.g., cellulose and similar bodies. By treatment with organic or inorganic acids, e.g., acetic, and heat, pectose changes to soluble pectin, and an abundance of calcium goes into solution. Therefore, Frémy asserts pectose to be a calcium compound of pectin. Mangin believes, however, that pectin is combined in the cell membrane with cellulose.

Frémy crushed unripe currants and extracted them several hours with distilled water, until the acid reaction disappeared. By acidifying

[1]The formation of pectin in fruits and vegetables, its extraction, purification, chemical and physical behavior, and use are dwelt upon at length because of the lack of any single work covering the field.

the currant residue with tartaric, malic, or sulphuric acid the solution became thick. Pectin went into solution.

Pectin was also formed when the fruit was cooked in its own juice because of the interaction of the fruit acid and the mother substance of pectin—pectose.

According to Bourquelot and Hérissey pectose may be converted into pectin by the action of an enzyme from *Aspergillus niger.*

Frémy's further researches showed that separated pectin consisted of loose wool-like white flakes, a tough, horny, somewhat elastic mass, or occasionally a hornlike powder. Its solution directs the ray of polarized light to the right. With water it forms first a sticky mass and finally with more water an opalescent colloidol solution. It is insoluble in alcohol and ether. The water solution upon the addition of alcohol becomes gelatinous, or pectin forms a flocculent precipitate. Acids do not coagulate the solution, but hydroxides of the alkaline-earth metals do. Ammonium sulphate or magnesium sulphate when added until saturation is near completion cause precipitation. Neutral lead acetate will not precipitate freshly prepared pectin but basic lead acetate will precipitate it.

If a pectin solution is cooked for a certain time, the addition of neutral lead acetate will cause precipitation, as pectin has been changed into its isomer parapectin. If pectin or parapectin is cooked with dilute acid for a certain time, it is changed to metapectin. This last isomer gives an acid reaction and is precipitated by barium chloride.

These three isomers of pectin may be distinguished through the percentage of lead in their respective precipitates. The pectin-lead precipitate contains 10 per cent of lead oxide, parapectin 19 per cent, and metapectin 33 per cent lead oxide.

Pectin is unusually sensitive to the alkalies and alkaline-earth metals. If a pectin solution has sodium hydroxide added to it and is acidified after a few minutes, a gelatinous precipitate occurs; pectin has been changed over to pectic acid. Ammonia will not cause this change (Braconnot).

Through the action of an enzyme, pectase, obtained in solution from carrot and beet roots, pectin may be changed into pectic acid. In obtaining this pectase the fresh sap of carrots was precipitated with alcohol, and the pectase-holding precipitate was dissolved in water. This solution when added to a solution of pectin will cause coagulation within a few minutes or half an hour. If the solution is sufficiently concentrated gelatinization occurs, while if dilute, flakes of pectic acid separate out.

Pectin and pectic acid were hydrolized by Bourquelot and Herissey by diastase (but not by ptyalin nor emulsin) into reducing sugars. The foregoing authors considered diastase as specific in bringing about this reaction.

According to Frémy, pectic acid is an isomer of pectin. They both form white powders after similar treatment, which swell in water and are easily soluble in hot water. Their water solutions react weakly acid, and form gelatinous precipitates with hard-metal salts. Alkalies and ammonia readily dissolve pectic acid. In acidified water pectic acid is less soluble than in pure water.

If pectic acid is heated a long time in water, it is changed into a soluble substance called parapectic acid. If a solution of pectic acid is heated an hour with a very slight excess of calcium hydroxide, it is converted into metapectic acid. A similar change occurs when pectic acid is heated for a long time with strong acids.

Metapectic acid has a syrupy consistency, is not precipitated by alcohol, its alkali and alkaline-earth salts are easily soluble, and it forms a lead salt with lead acetate.

Mulder considered the formula of pectic acid as $C_6H_8O_5$. Regnauld ascribed to the same body $C_{11}H_{14}O_{10}$. Fromberg's result is similar to Mulder's except the size of the molecule is doubled. Berzelius, who refers to the work of Fromberg, gives the following formulas: for pectin $C_{24}H_{32}O_{20}$, for pectic acid $C_{12}H_{16}O_{10}$, and for the metapectic acid $C_6H_8O_5$.

Chodnew gives $C_{28}H_{42}O_{24}$ as the formula for pectin. He describes a rational method for obtaining pectic acid from turnips, in which pectin is not isolated first, but pectose is changed directly to pectic acid. Finely ground turnips are heated with very dilute potassium hydroxide. The potassium salt of pectic acid is found in the filtrate. From this salt gelatinous pectic acid may be obtained through the action of mineral acids.

An acid from pectin is also obtained by Chodnew from turnips. The ground and washed turnips are cooked in a very dilute solution of hydrochloric acid, and alcohol is added to form a precipitate. It is evident that this precipitate must be pectin itself.

After extracting with dilute hydrochloric acid, Chodnew heats the turnip residue with potassium hydroxide, and again obtains a gelatinous substance which he calls hyperpectic acid. Unripe fruit does not contain pectin but pectic acid, bound with calcium. Through reduction of this during ripening pectin is formed.

Chodnew gives the following formulas:

Pectin-like cell tissue	$C_{28}H_{44}O_{22}$
Pectin	$C_{28}H_{42}O_{24}$
Pectin acid (hydrous)	$C_{28}H_{42}O_{25}$
Pectic acid	$C_{28}H_{40}O_{26}$
Hyperpectic acid	$C_{28}H_{38}O_{27}$

The authors mentioned relied for their formulas mostly upon the analysis of lead, silver, and barium salts and also upon the free substances.

The metapectic acid from turnips was investigated by Scheibler. He holds that by heating it with strong acids it is split into a sugar and an acid. The sugar from metapectic acid, pectin sugar or pectinose, is identical with arabinose, which Scheibler extracted from gum arabic. Metapectic acid, therefore, is nothing else than arabin; Frémy's formula $C_8H_{14}O_9$ must be incorrect. Later Scheibler finds that his metapectic acid from turnips is not a substance of the pectin group, but arabin, which is in the insoluble form of meta-arabic acid in the turnip.

Reichardt considers pectin bodies as gelatinous carbohydrates, and holds them quite similar to gums.

Herzfeldt discovered that upon hydrolysis pectin bodies left arabinose and by oxidation with nitric acid gave mucic acid. The last result is due to the presence of a galactose group.

Parapectic acid from turnips gave 29.6 per cent mucic acid and 14 per cent furfurol. It is evidently not one substance but a mixture of arabinose and galactose. The percentage composition of these two sugars is not constant.

In regard to the constitution of pectin bodies, Cross gives the following: Pectin contains 40.8–43.5 per cent carbon and 56.6–57 per cent hydrogen, except currant pectin which has a richer content of both.

The substances of the oxycellulose group lie in the same field. The same proportions are also given by lignocellulose. Pectin reacts similarly to lignocellulose with chlorine and forms chinochloride which through reduction changes to a derivative of pyrogallol. Cross considers pectin as a soluble lignocellulose.

Tromp de Hass and Tollens consider the question of the position of pectin from a new angle. Pectin compounds are frequently acidic in their reaction, while plant slimes are neutral. The last are carbohydrates whose constitution contains H : O = 1 : 8. For pectin the proportion was about 1 : 7.4–8.4.

Tollens' results were slightly high in oxygen but this may have been due to impurities. The excess of oxygen may probably have been caused by acidic or basic substances joined to the pectin bodies. They may perhaps take on in that way one or more anhydrous or esterized carboxyl groups.

Presumably, the ester-forming carboxyl group may be attached to the CHO— or CH_2OH— group of the carbohydrate, or possibly it may be part of a five carbon atom acid, the formula for which would be $(C_5H_8O_4)$, $C_5H_8O_5$; or C_5— and C_6— groups could similarly be attached.

As O'Sullivan considers the occurrence of a combination of carbohydrates and acids in the gums, so Tollens considers pectin. Arabic acid has according to O'Sullivan the formula $C_{91}H_{142}O_{74}$ and leaves besides glucose geddin acid $C_{23}H_{38}O_{22}$. In arabic acid the relation of H : O = 1 : 8.33 and in geddin acid H : O = 1 : 9.26. The original pectin is neutral because the acid group appears in it in a lactone or ester form. By treating with alkalies the anhydride binding will first break and the pectin will be changed to pectic acid and form a salt with the alkali. By hydrolysis hexoses, pentoses, and acids result.

MICROCHEMICAL REACTIONS

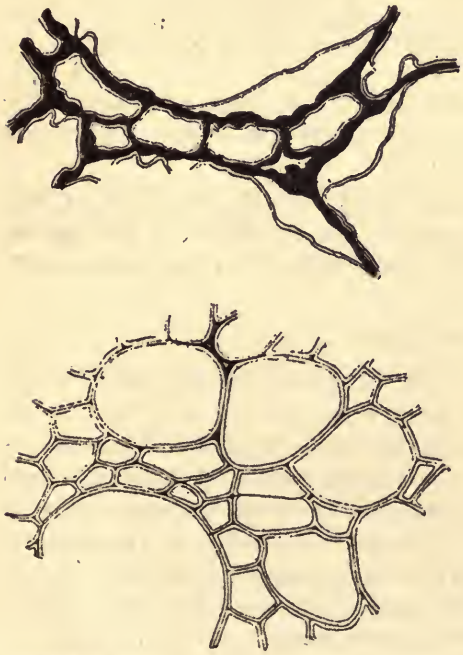
The fact that pectin substances are akin to cellulose, and occur in conjunction with it, renders its identification by microchemical means somewhat difficult. Mangin more particularly has investigated these matters, and gives the following methods:

1. Methylene blue, Bismarck brown, and fuchsine stain pectic substances, lignified and suberized walls, but not pure cellulose. If sections thus stained are treated with alcohol, glycerine, or dilute acids, the lignified or suberized walls retain their coloration, while the pectic substances are decolorized with rapidity.

2. Croceine and bigrosine stain lignified and suberized walls, but do not stain pectic compounds.

3. Croceine, naphthol black, and orseille red stain pure cellulose, but do not stain pectic substances; similarly, pectic compounds are unstained by Congo red and azo blue, while cellulose and callose are.

4. The middle lamella, which apparently consists of compounds of pectic acid, may be differentiated from the other pectic substances which are mixed with the cellulose of the cell walls by the following method: A thin section is placed in a 20–25 per cent solution of hydrochloric acid in alcohol for twenty-four hours; the section is then washed with water and treated with methylene blue or phenosafranin. The middle lamella stains much more deeply than the rest of the wall.



(Rosenberg-Hein)

Fig. 11.—Pectin (black) in intercellular spaces.

5. If, after the foregoing treatment with acid alcohol, the section be washed in a 10 per cent solution of ammonia, it is found that the cells separate with ease one from the other. According to Mangin, the combined pectic acid is freed from its bases by the treatment with acid alcohol, and is then dissolved by the ammonia. A recombination of the pectic acid may be brought about by treatment with baryta water, and after this process the cells will not separate one from the other.

6. The cellulose may be separated in the following manner: A thin section is treated with cuprammonia for twenty-four hours; it is then washed, first with water,

and, finally, with 2 per cent solution of acetic acid. The cellulose is thus dissolved and fills the cells and intercellular spaces. On treatment with chlorzinc-iodide the middle lamella gives either no color reaction or turns a pale yellow, while the cellulose gives the familiar blue reaction; the membrane stains very deeply with safranin or methylene blue, and is easily soluble in a solution of ammonia.

Rosenberg found that some of the basic dyestuffs as safranin, methylene blue, neutral violet, and ruthenium red (ruthenium sesquichloride) were able to color pectin in unripe fruit without coloring the remainder of the fruit.

But for ripe fruit another test was necessary: concentrated sugar solution was placed on the fruit section and the entire heated. If pectin had been present in the intercellular substances it was lost, its place filled with air, the cell walls distorted and separated from one another. The pectin accumulation filled the intercellular space as a gelatinous mass which upon exposure to air darkened to black.

Pectin is never found in the inside of a cell or on the inside of the cell wall but always on the outside. Most of the intercellular spaces are lined with pectin. This lining is continuous with the middle lamella and appears in the first development.

The gelifying pectin is not the first of the pectin bodies to appear in the intercellular substance but is seen only during ripening. It is soon replaced by calcium pectate which marks the end of the pectin series.

There is much confusion in the literature of pectin substances. The older authors described a large number of different bodies using various terms.

The following terminology will be used for the remainder of consideration of the pectins: (1) pectose, the equivalent of protopectin; (2) pectin, under which designation parapectin falls; (3) pectic acid.

PROTOPECTIN

Under protopectin may be designated pectose, which exists in unripe or barely ripe fruit (but not in over-ripe or decayed fruit) as an insoluble substance, which through ripening is transformed into pectin. Through heating with water, or still better with weak acids, this conversion is accelerated. Bourquelot and Hérissey obtained pectin by heating protopectin in alcohol. Protopectin according to Tschirch and Rosenberg is colored with basic dyes and appears as the outer coat of the intercellular covering and the middle lamella of the fruit. Rosenberg considered it as pectin in his dissertation.

Frémy considered tenable the possibility that protopectin is a union of pectin and calcium, a calcium pectinate. Other investigators as Payen and Mangin speak of calcium pectate, i.e., a compound of pectic

acid and calcium. The latter conception is not correct as pectic acid is a decomposition product of pectin and not a precedent.

In order to decide whether or not protopectin is a combination of calcium and pectin the following experiments were conducted by von Fellenberg.

Two kg. of apples were cooked with water and pressed. The residue was then cooked one-half hour with 1 kg. of 50 per cent sugar solution to separate water-insoluble but sugar-soluble pectin bodies. The residue was washed with water; 42 gm. of gray, protopectin powder were obtained. This gave by Zeisel's method 2.12 per cent methyl alcohol in comparison to apple pectin which contains 10.5 per cent methyl alcohol.

Ten gm. of this protopectin was cooked one-half hour with 150 c.c. water and pressed. The filtrate was centrifuged until clear. HCl was added, alcohol added until precipitation was complete, precipitate pressed and dried. The resultant dried pectin contained: 0.440 gm. pectin and 0.010 calcium or 100 parts pectin to 2.3 parts calcium by titration.

Another portion of protopectin was cooked in a 2 per cent acetic acid solution, filtered, pressed, washed with water, and filtrate and wash water concentrated in vacuum. The analysis of calcium and pectin in this sample gave results as follows: 0.004 gm. pectin and 0.080 gm. calcium; 100 parts pectin to 2,000 parts calcium.

A third portion of protopectin was treated with 150 c.c. of 1 per cent hydrochloride acid in the cold and pressed. The solution gave 0.069 gm. pectin and 0.012 gm. calcium; 100 parts pectin to 1,733 parts calcium.

It is evident, therefore, that the combined calcium is soluble in cold acetic acid. Acetic acid has no effect on protopectin. The principal part of the calcium is therefore not united with the pectin, but is a water-insoluble calcium salt. On account of the colloidal nature of protopectin it is unlikely that a part of the calcium lost through acetic acid was held back by absorption. This is especially doubtful since the protopectin had just been treated with the stronger hydrochloric acid. It has been shown further that protopectin is not combined with any metal. Concentrated acids do not split protopectin into pectin, although this may possibly be accomplished by hydrolysis with dilute acids. In the formation of pectin from protopectin, no reducing sugar is formed, therefore it is not a glucoside.

PECTIN

Many methods for obtaining pectin are found in literature. It was first obtained by Braconnot and Frémy as a precipitate from clear, filtered fruit juice upon the addition of a double volume of alcohol. The pectin is precipitated in a gelatinous mass. By filtering through linen or canvas, pressing out, and drying, it can be obtained as a horny or flaky, more or less colored, mass. It can be freed from minerals by dissolving in water, filtering several times, adding hydrochloric acid, and again precipitating with alcohol.

This original method is unsatisfactory for three reasons. First, it is difficult to get a clear filtrate of many fruit juices, e.g., currants.

Filtration requires a long time. Secondly, the pectin obtained in this way contains impurities, among them coloring matter. Thirdly, in this way only the free pectin in the juice is secured, since as a rule the larger part of pectin is in the form of protopectin.

Another method resorted to in pectin purification is that of dialysis. The fruit jelly is first dialyzed. The colloidal residue is then precipitated with alcohol. Dialysis, however, does not remove much of the coloring matter or tannin. Dialysis is much more effective when combined with other methods of purification such as acids and salts. Pectin itself diffuses but very slightly through the membrane.

The best-known method for pectin purification is that of Bourquelot and Hérissey. By this method all the alcoholic soluble impurities are first removed by extraction with alcohol. During this extraction a large part of protopectin is converted into pectin. The material is now heated under pressure with water and the filtrate precipitated with alcohol.

Until recently the known constituents of pectin have been confined to arabinose and galactose. These were hydrolysis products of pectin. Mucic acid was also obtained from pectin by oxidation with HNO_3.

Von Fellenberg discovered methyl alcohol as another constituent. The alcohol is so loosely bound that large amounts are easily split off in a minute by the action of alkalies. Pectin by this reaction is changed to pectic acid. Acids do not split off methyl alcohol as easily as alkalies.

Von Fellenberg certifies to the existence of another pectin constituent, methyl pectose. By the Tollens method of pentose examination phloroglucin is obtained, which is soluble in alcohol giving a brown color. The soluble portion has many similarities to methylfurfurolphloroglucin. The exact nature of the methylpentose is at present unknown.

According to the investigations of Tollens the pectin molecule consists of an ester or anhydride containing a carboxyl group, in which the carboxyl group has the position of an esterized CHO— or CH_2OH— group of the carbohydrate. The splitting-off of methyl alcohol through the action of sodium hydroxide and the formation of an acid may also be due to the ester formation. Von Fellenberg considers pectin, therefore, as a methyl ester of pectic acid. The statement of Frémy that pectin, pectic acid, and metapectic acid are isomers or polymers is not in accord with the foregoing experiments.

To ascertain whether methyl alcohol and no other alcohol was present the methoxyl was estimated by two methods: first by Zeisel's and secondly by the colorimetric method of Denigès. Zeisel's method consists in estimating the methoxyl groups by decomposing the substance with strong hydriodic acid and eliminating the alkyl group as alkyl iodide. The alkyl iodide is passed through an alcoholic solution of silver nitrate, which decomposes the alkyl iodide and the silver iodide is weighed:

$$R \cdot OCH_3 + HI = R \cdot OH + CH_3I.$$

This method, however, does not eliminate error from the possible presence of other alcohols besides methyl.

By Denigès' method the alcohol is oxidized to aldehyde, and estimated with acid fuchsin. The formaldehyde frees fuchsin, while of the aldehydes from other alcohols only amyl and isobutyl give a minimum color.

Both Denigès' and Zeisel's method were tried on currant pectin. The pectin was obtained by precipitation from the filtered juice with alcohol, and while not very pure it was pure enough for the experiment. It contained 2.9 per cent ash and contained 9.3 per cent methyl alcohol by Zeisel's method (determined as ash-free substance) and 9.3 per cent by Denigès'. This would indicate that methyl alcohol was the only alcohol in pectin.

Orange pectin.—2.3 kg. oranges were boiled in a reflux condenser six to eight times (twenty-minute periods) with 4 to 6 liters of 95 per cent alcohol. This process tended to free them from coloring matter, acids, etc. Between each boiling the material was pressed. Three liters of water were added to the final press cake and the mixture heated in an autoclave for an hour at 110°C. At the end of this period the contents were pressed and the liquid filtered until clear. The pectin was obtained from the filtrate by adding a double volume of alcohol to which 7 c.c. of concentrated hydrochloric acid had been added per liter. The coagulum was pressed in a cloth and kneaded in several changes of alcohol until the acid reaction disappeared. Finally the pectin was washed with ether and dried in a vacuum desiccator over sulphuric acid. In this way 17 gm. of a white, feathery pectin were obtained. When analyzed it gave the following:

Ash 0.2 per cent.

Methyoxyl estimation gave: 0.2495 gm. substance gave 0.2095 gm. Ag I = 11.44 per cent methyl alcohol; 0.2134 gm. substance gave 0.1851 gm. Ag I = 11.76 per cent methyl alcohol.

The pentose estimation gave: 0.2749 gm. substance gave 0.1048 gm. phloroglucid; alcohol extracted therefrom 0.0060 gm. methylfurfurolphloroglucid. Hence there was present 0.1126 gm. arabinose or 41.0 per cent arabinose and 0.0185 gm. methyl pentose or 6.7 per cent methyl pentose.

Estimation of galactose: 0.5 gm. lactose and pectin when treated similarly yielded mucic acid. Both samples of mucic acid melted at 215°C. (uncorr.) and solidified at 218°C. 0.5 gm. lactose = 0.25 gm. galactose gave 0.1484 gm. mucic acid; 0.5 gm. pectin gave 0.1626 gm. mucic acid.

Assuming that the galactose of pectin had formed mucic acid similarly to the galatose of lactose, the galactose content of pectin is 54.8 per cent.

It is possible that as plants have specific proteins, so each plant may have a pectin of different and specific chemical composition. The pectin is such a complex molecule that the existence of very many pectins is easily possible. The pectin molecule apparently contains pentoses, methyl pentoses, mucic acid-forming groups, carboxyl groups, and methoxyl groups. These various constituents might readily occur in various numbers and in various different arrangements.

TABLE XII

SOURCES AND PROPERTIES OF PROTOPECTIN, PECTIN, AND PECTIC ACID

	SOURCES	COMPOSITION	SOLUBILITY	REACTIONS						
				Ammonia	Sodium Hydroxide	Electrolytes	Tannin	Albumen	Dyestuffs	Jelly-Making
Protopectin..	In unripe fruits and tubers	Chemical constituents the same as those of pectin	Insoluble in water. No soluble known	No reaction	Changes quickly in the cold to pectic acid				Colored by basic, but not by acidic coloring matters	Gives no jelly when cooked with sugar and pectin-free fruit juice
Pectin= methyl ester of pectic acid	In ripe fruits	Oranges which form mucic acid, arabinose methyl pentose, carboxyl groups, alcohol	Colloidal solution, insoluble in alcohol, etc.	No reaction	Changes quickly in the cold to pectic acid	Not sensitive to electricity. Will coagulate by: $CaSO_4$, $PbNO_3$, basic lead acetate; neutral lead acetate, $FeCl_3$, and $SnCl_2$; after standing for some time. Will not coagulate by: NaCl, $CaCl_2$, $SrCl_2$, $BaCl_2$, $MgCl_2$, $AlCl_3$, $FeSO_4$, $CO(NO_3)_2$, $NiSO_4$, $CdCl_2$, $ZnSO_4$, $MnCl_2$, $AgNO_3$, $HgCl_2$. Will coagulate and change to salts of pectic acid through $Ca(OH)_2$, $Ba(OH)_2$	Will not coagulate	Will not coagulate	It is coagulated by either basic or acidic dyestuffs	Gives a jelly when cooked with pectin-free fruit juice. Gives a poorer jelly with sugar and organic calcium salts
Pectic acid..	In oranges and other fruits	Oranges which form mucic acid, arabinose, methyl pentose, carboxyl groups. No methyl alcohol	Forms with difficulty colloidal solutions in H_2O. Insoluble in alcohol, ether, benzol	Easily soluble as ammonia salts	Easily soluble as sodium salts	Very sensitive electrically. Will coagulate through: Mineral acids, $Ca(OH)_2$, $Ba(OH)_2$, NaCl, $CaCl_2$, $SrCl_2$, $BaCl_2$, $MgCl_2$, $AlCl_3$ $FeSO_4$, $FeCl_3$, $CuSO_4$, $Co(NO_3)_2$, $NiSO_4$, $CdCl_2$, $ZnSO_4$, $SnCl_2$, $MnCl_2$, $AgNO_3$, $PbNO_3$. Will not coagulate through $HgCl_2$	Will not coagulate	Will not coagulate	It is coagulated by basic dyestuffs but not by acidic dyestuffs	Gives no jelly when cooked with pectin-free fruit juice. Effects a spontaneous coagulation of fruit juice by formation from pectin by enzymal pectose

If the results of the analysis of orange pectin be added in the form of their anhydrides we have the following:

41.0 per cent arabinose	= 36.1 per cent	araban
6.7 per cent methyl pentose	= 6.0 per cent	methyl pentosan
54.8 per cent galactose	= 49.3 per cent	galactan
11.5 per cent methyl alcohol	= 11.5 per cent	methyl alcohol
	102.7 per cent	

The methyl alcohol is considered as such and not as methylene. This calculation does not take into account the effect of the introduction of a carboxyl in a sugar molecule.

Physical behavior of pectin.—Pectin is a reversible colloid, soluble in water, forming an opalescent solution. It shows Brownian movement. It is precipitated from solution by concentrated alcohol as a gelatinous mass, and by dilute alcohol as flakes.

Besides alcohol some of the metal salts coagulate pectin. Turnip, apple, and quince pectin are precipitated by copper sulphate, lead nitrate, and basic and neutral lead acetate. Turnip and quince pectin are precipitated by ferric chloride while a fresh solution of apple pectin remains clear when treated with this reagent. After standing one hour, however, coagulation occurs in this case also. Zinc chloride when added to a fresh solution of turnip pectin causes precipitation. Quince pectin after standing for some time with zinc chloride forms a precipitate.

Entirely analogous behavior was noticed by Frémy in lead acetate precipitation. He considered pectins from different fruits isomeric. Today it is considered that the similarity is physical not chemical. Possibly the particles of pectin become larger upon standing in water solution. When the particles attain a sufficiently large size they are subject to coagulation by metal salts which had no action at first.

Neutral lead acetate may also be placed under the same category as the metal salts in relation to coagulation. When the solution is of pectin a month old, precipitation occurs, but not in all cases where fresh pectin is used. The freshly separated pectin will often not be precipitated by neutral lead acetate but will be precipitated by basic lead acetate. Investigations have been carried on to ascertain the difference between pectin which was not precipitated by lead acetate and its isomer parapectin which was coagulated. Difference in physical behavior is not always accompanied by difference in chemical constitution.

Pectin is not coagulated by the following metal salts: $AgNO_3$, $HgCl_2$, $CO(NO_3)_2$, $SrCl_2$, $BaCl_2$; nor by salts of the alkalies. Coagulation with the above-named salts is reversible; by acidifying, precipitation occurs, but the addition of ammonia causes solution. When precipitation occurs by the addition of $CuSO_4$, further addition of ammonia causes solution and the formation of a complex blue copper salt. If precipitation be caused by ferric chloride, added ammonia allows the precipitate to remain, and iron precipitates also as hydroxide. However, this is only the case when a great excess of ferric chloride is present. If in only a very slight excess, a clear solution forms, and the ferric hydroxide remains in colloidal solution in which the pectin is held. When the lead nitrate coagulum is made

alkaline with ammonia, easily soluble basic lead nitrate is formed. This in itself forms a gelatinous substance and prevents the solution of the pectin.

The old investigators considered the combination of pectin and metal salts precipitants as chemical. The chemical compound is very weak, if any, as the reaction of pectin and the ready reversibility of the coagulum attest. This coagulation is more electrolytic, analogous to the coagulation of some other colloids with metal salts.[1]

Pectin is not precipitated by tannin nor albumen, nor by acid or basic dyes.

A gelatinous precipitate forms when calcium or barium hydroxide is added to a pectin solution. The hydroxyl ion has changed pectin into pectic acid, and calcium or barium pectate forms. Acids free the pectic acid by combining with the metals.

Pectin as has already been stated is a methyl ester of pectic acid. Consequently if pectin be treated with sodium hydroxide, methyl alcohol is split off. This separation approaches more nearly the theoretical amount when the solution has been heated. The following experiments show this:

When a 5 per cent solution of quince pectin was used, the methyl alcohol content by Zeisel's method was found to be 10.05 per cent. Therefore,

a normal pectin solution corresponds to $\frac{100.32}{10.05} = 318.4$ gm. of pectin per liter or 1 gm. pectin $= \frac{1000}{318} = 3.14$ c.c. N/1 NaOH or 5 c.c. of the .5 per cent solution of pectin = .0785 c.c. N/1 NaOH.

Five c.c. of pectin solution were used in each case—different amounts of N/1 NaOH used for different definite times. They were brought back to acid reaction with N/1 HCl and diluted with 5 c.c. water, then distilled and the methyl alcohol determined in the distillate. The first 4 c.c. carried all of the methyl alcohol liberated. The methyl alcohol was determined by Denigès' method.

The results showed that in a 5 per cent solution of quince pectin all the pectin was hydrolyzed to pectic acid and methyl alcohol by heating (for 5 c.c. this was .0785; .08 c.c. N/1 NaOH was used). Double the theoretical amount of N/1 NaOH hydrolyzed it completely in five minutes in the cold, while four times the theoretical amount hydrolyzed it completely in two minutes in the cold.

[1]Tartar and Gailey ("Rôle of H-ion Concentration in the Precipitation of Colloids," *Journal of the American Chemical Society*, XIV [1922], 2212) report that the addition of neutral salts to solutions of colloids, results in jelly formation at much lower hydrogen ion concentration than colloidal isoelectric points. Halliday and Bailey ("Effect of Calcium Chloride on Acid-Sugar-Pectin Gels," (*Journal of Industrial and Engineering Chemistry*, XVI [1924], 595) have shown that the addition of $CaCl_2$ in this connection to pectin jellies acts in this way and if increased sufficiently may cause syneresis. Tarr ("Fruit Jellies No. 1, The Rôle of Acids," *Delaware Agricultural Experiment Station Bulletin*, No. 134, Tech. No. 2, 1923) showed that syneresis and precipitation of pectin occurs in pectin jellies at pH's above 3.1.

PECTASE

Action of pectase.—The pectase of turnip juice was precipitated by alcohol and dried. This dried pectase (with adherent pectin) was added to boiled pear juice. On the following day coagulation had taken place. On distillation it gave a strong Denigès' methyl alcohol reaction. Heated juice which had not had pectase added to it gave no methyl alcohol reaction. The distillate of the natural juice on standing without heating gave a methyl alcohol reaction.

An apple coated with paraffin and allowed to stand turned brown inside. When the juice was distilled the distillate gave the reaction for methyl alcohol.

It was also shown that juice which had started to ferment contained methyl alcohol from pectin.

Decayed apples contain no protopectin, but reduced amounts of pectin and large amounts of pectic acid and methyl alcohol.

The enzyme which causes the coagulation of vegetable saps containing pectin was discovered by Frémy in 1840. At present there is a certain amount of confusion in the terminology of this and related enzymes. Euler applies the name pectase to the enzyme which converts pectose into pectin, and calls the enzyme which coagulates pectin, pectinase. Other writers retain the original name pectase for the enzyme which coagulates pectin, and in the following account this enzyme will be denoted by this name. With regard to the two other related enzymes, the most generally accepted terminology seems to be that in which the enzyme which hydrolyzes pectin to *d*-galactose and *l*-arabinose is called pectinase, and the enzyme which converts pectose into pectin, pectosinase.

Previous workers on this subject—Frémy, Bertrand, Mallèvre, Bourquelot, and Bourquelot and Hérissey simply allowed coagulation of the pectin by the enzyme to take place under various conditions, and noted the time taken before this was complete.

In the research by N. G. Ball an attempt was made to study the action of pectase by observing the electrical conductivity of a solution of pectin when acted upon by the enzyme, and also by determining the change in viscosity.

The pectin used in this research was obtained exclusively from the roots of the carrot, *Daucus carota.* The first extraction was based on a method suggested in C. A. Browne's *Handbook of Sugar Analysis* for obtaining pectin from the juice of ripe pears. The chopped-up carrots were put into a can and steamed in a Koch's sterilizer for about forty-five minutes, and the juice was then squeezed out and filtered under reduced pressure. A little oxalic acid was added to precipitate calcium, and a little tannic acid to precipitate albumins. The juice was filtered, and centrifuged until almost clear. The pectin was precipitated by addition of an equal volume of alcohol, and was filtered off and redissolved by pouring a little hot water onto the filter. The pectin was subsequently reprecipitated by addition of alcohol, and the gelatinous precipitate obtained was collected by means of a centrifuge and dried on a watch glass placed on a water bath. A horny residue was obtained in this way, and about 0.3 gm. of pectin was extracted from about 1100 gm. of carrots.

In subsequent extractions the carrot roots were finely minced, and the pulp covered with water and heated on a water bath for one or two hours. The pulp was then squeezed, and the liquid obtained was treated as before. This method was based on one described by Bourquelot and Hérissey, who obtained pectin by heating chopped-up gentian roots with water in an autoclave at 110°C.

Browne recommends the addition of tannic acid to juice which has been extracted in the cold. In cases where the carrot pulp had been heated this was found to be unnecessary, as all albuminous substances had been coagulated.

The pectin obtained from these various extractions was dissolved in sufficient water to form a 2 per cent solution, and a few drops of toluene were added to prevent growth of micro-organisms. The pectin solution thus obtained was in a fairly pure state, but was faintly acid to litmus paper. In all the experiments this solution was diluted with an equal quantity of water.

Sap released from the leaves of *Syringa vulgaris* was used as a source of pectase. This plant was chosen both for the sake of convenience, as the leaves could be obtained easily, and also owing to the fact that Bertrand and Mallèvre state that sap pressed from these leaves is fairly active in coagulating pectin.

The method of extraction was as follows: Leaves were stripped from fresh shoots of *Syringa,* the petiole of each leaf being removed. They were then placed in a small steel cylinder fitted with a piston, and provided with a hole at its lower end. The piston was squeezed in by means of a vice, and the expressed sap was centrifuged until clear, and was then ready for use.

a) *Measurement of the electrical conductivity during the coagulation of pectin.*—If the product of the action of pectase on pectin is a true gel, there would be little change in electrical conductivity during its formation, as the resistance of a gel to the passage of ions is practically the same as that of the sol from which it has been formed. One c.c. of distilled water was added to 1 c.c. of 2 per cent pectin solution in a test tube, and 1 c.c. of freshly extracted sap from the leaves of *Syringa* was put into a similar tube. The two tubes were partly immersed in a large glass tank of water for about ten minutes, in order that their contents might come to the same temperature. At a noted time the contents of the tubes were mixed and the mixture poured into a Hamburger conductivity tube, which was also immersed in the same tank of water at 13°C. Measurements of the resistance of the mixture were made every ten minutes by comparison with a standard resistance, using a meter bridge with an alternating current and telephone.

The resistance of the mixture remained practically constant for over two hours, and at the end of this time a solid jelly had been formed in the conductivity tube. During the experiment the temperature of the water in the tank was constant within 0.5°C.

The product of the action of pectase, therefore, consists of a spongy network composed of a more or less solid phase in the meshes of which a more liquid phase is distributed.

b) *Measurement of the change in viscosity.*—In order to measure the change in viscosity, a viscosimeter of the Ostwald type was constructed. this consisted of a U-tube made of glass tubing. Part of one limb was composed of a piece of thermometer tubing, and above this capillary the tube was dilated into a small bulb. Three c.c. was the amount of liquid which was always used, and this was introduced by means of a pipette. In use, the liquid was sucked up to a definite height above the bulb in the limb of the U-tube which contained the capillary, and was then allowed to run back. The time taken by the meniscus in passing between marks on two constrictions above and below the bulb was determined by means of a stopwatch. As this piece of apparatus was not sufficiently accurate to permit absolute determinations of the viscosity being made, the times taken for the meniscus to pass between the two marks were compared with one another.

In the experiments at a temperature above 0°C. the viscosimeter was partly immersed in a tank of water containing about 20 liters. This was kept at a constant temperature by the introduction of either hot or cold water from a tap connected with another tank. The water in the tank was kept well stirred, and a sensitive thermometer attached to the viscosimeter was easily maintained within 0.1°C. of any desired temperature.

The viscosimeter was standardized with 3 c.c. of distilled water at 0°C., and the time for emptying the bulb was 3.0 seconds.

These experiments show that the product of action of pectase on pectin has the structure of a gel composed of a semi-solid reticulum, in the meshes of which a liquid is distributed, and also that the gel, when formed, is broken up in the presence of electrolytes by the clumping of the more solid portion into separate aggregates.

It appears that what has hitherto been described as the coagulum formed by the action of pectase is composed of calcium pectate, and not of pectic acid, as previously stated by Frémy. They base this conclusion on the fact that the coagulum is completely insoluble in feeble alkaline liquids, but dissolves almost instantaneously after having been macerated in dilute hydrochloric acid, and the resulting solution is found to contain calcium. They also state that if juice, extracted from carrots, which has been decalcified by addition of oxalic acid, be added to a solution of pectin from which calcium has been carefully removed, the mixture remains indefinitely liquid, but the least addition of a soluble calcium salt causes rapid coagulation. They point out that, owing to the very high molecular weight of the pectic compounds, and to the enormous volume which they occupy in the gelatinous state, the amount of calcium required for the formation of a coagulum consisting of calcium pectate would be very small.

In view of the results obtained in the experiments, it seems possible that the calcium or other metallic ions act in a purely physical manner in causing coagulation. In this experiment sap was extracted from the leaves, and the enzymes precipitated by the addition of five times its volume of alcohol. The precipitated enzymes were redissolved in water, and added to pectin solution, from which dissolved calcium salts were absent. In this way any electrolytes, including calcium salts, would have been almost com-

pletely removed. The experiment, therefore, affords no evidence that the gel which is formed is composed of calcium pectate.

If the statement of Bertrand and Mallèvre is correct, namely, that in the absence of calcium salts a mixture of pectase and pectin remains indefinitely liquid, then it would seem that gelification, as well as coagulation, is due to a minute trace of electrolytes. As far as gelification is concerned, the action of the electrolytes is possibly indirect, and it may be that their presence is necessary in order to allow the enzyme to exert its activity.

If this is the case, then possibly the events which take place during the coagulation of pectin are somewhat as follows: Under the action of pectase some kind of pectic acid is produced from the pectin. If electrolytes are completely absent, the mixture remains liquid; but if any ions are present, and especially if they belong to one of the divalent metals such as calcium, partial precipitation of the colloid takes place. At first these colloidal particles will be free from one another, and while this is the case the viscosity will remain almost constant, thus explaining the first portion of the curves. As the action of the pectase proceeds, and more material is formed, which can be precipitated by the electrolytes, a semi-solid reticulum is gradually built up with a consequent rise in viscosity. As the reticulum becomes denser, the viscosity will increase rapidly; but if electrolytes are present in larger proportion, or if they are allowed to act for a sufficiently long time, clumping together of the particles of colloid forming the reticulum of the gel takes place, and a suspension is formed with a consequent dimunition in viscosity. A maximum viscosity will be reached when the rate of gel-formation becomes insufficient to counterbalance the clumping effect.

PECTIC ACID

Pectic acid may be obtained by taking about 100 c.c. of .5–1 per cent pectin solution, adding 5 c.c. of 10 per cent NaOH and allowing to stand two minutes. Then acidify with HCl, filter off the gelatinous precipitate through a cloth, press out, wash several times with alcohol until all the HCl is removed, wash with ether, and dry in a desiccator over sulphuric acid. It may also be obtained by heating the fruit under pressure in an autoclave in order to change protopectin and pectin into pectic acid.

Weighed pectin was hydrolyzed with NaOH, neutralized with HCl, dried to constant weight in a glycerine drying oven at 103°C., weighed, and the NaCl determined and subtracted. Pectic acid was found in the proportion of 95.16 gm. acid to the total weight of pectin. .2484 gm. pectin gave .2364 gm. pectic acid. By the direct distillation of hydrolyzed pectin 10.54 per cent of methyl alcohol was found (the equivalent of 4.62 per cent of CH_2) which proves up very well with 4.83 per cent by the indirect estimation noted above. It is quite evident, therefore, that pectin contains no other alcohol but methyl or otherwise these two results would not agree so closely.

One hundred gm. of pectin acid is theoretically equivalent to .35 gm. H according to the amount of methyl alcohol contained in apple pectin—

10.5 per cent. By titration its equivalent is .43 gm. H per 100 gm. pectic acid.

Orange pectin contains 11.7 methyl alcohol. Therefore 100 gm. of pectic acid from oranges should equal .42 gm. NaOH. By actual titration with phenolphthalein as an indicator the pectic acid equivalent is .46 gm. H per 100 gm. pectic acid. This excess may be due to the breaking down of a lactone group by the NaOH. The freed COOH group may combine loosely with NaOH. This latter combination is easily broken upon acidification.

The pectic acid molecule takes up one-half molecule of water. Barium pectate contains 22.5–23 per cent Ba. Copper pectate contains 9.78 per cent Cu.

The solubility of pectic acid is greatly influenced by small amounts of electrolytes. The white pectic acid powder is soluble in water and forms a colloidal solution of smaller particles than those of pectin solution.

Pectic acid is precipitated by most metal salts, e.g.: NaCl, $CaCl_2$, $SrCl_2$, $BaCl_2$, $MgCl_2$, $AlCl_2$, $FeSO_4$, $FeCl_3$, $CuSO_4$, $CO(NO_3)_2$, $NiSO_4$, $CdCl_2$, $ZnSO_4$, $SnCl_2$, $MnCl_3$, $AgNO_3$, $PbNO_3$, etc. It is not precipitated by $HgCl_2$.

In accordance with its character as a negative hydrosel, pectic acid is precipitated by albumin but not by tannin. The basic dyes, e.g., fuchsine, crystal violet, methylene blue, bismarck brown, safranin, precipitate pectic acid in intensely colored flakes. Pectin is unaffected by these dyes. Acid dyes as eosin, picric acid, azolithmin, and curcumin form no precipitate; neither do Congo or indigo carmin.

THE FORMATION OF FRUIT JELLY

Just what chemical substances are necessary and how they combine to form a fruit jelly of the proper consistency has been a subject of much investigation and discussion.

Frémy claimed that jelly formed from a change of pectin into pectic acid. He considered pectic acid the essential part of jelly, as fruit juice spontaneously gelatinized when pectin was transformed to pectic acid by the action of an enzyme pectase. This jelly, however, has no connection with fruit jelly for three reasons, viz.: (1) When a pectic acid solution and sugar are mixed no jelly forms. (2) Pectic acid together with sugar and another acid or salt gives a syrupy liquid. A jelly of the proper consistency does not form because pectic acid is not soluble in this media. (3) An analysis of fruit jelly does not disclose any pectic acid.

Tschirch experimented with currants. He considered jelly as due to a pectin and sugar solution or a combination between pectin and sugar. Without sugar he could obtain no jelly. As a disproof of this theory we have the experience of von Fellenberg. Upon dialyzing currant jelly, he observed that it attracted water quickly. The liquid increased in the apparatus and in fifteen hours the jelly dissolved. No clear solution resulted; flocks of a body similar to cellulose remained which could be removed by filter or centrifuge. When the clear filtrate was dialyzed, flocks were formed during dialysis which were not present beforehand in

the jelly. These flocks dissolved in a sugar solution, and on successive heating and cooling a jelly formed. These flocks were considered by Tschirch as pectin. But this substance is not taken as pectin by von Fellenberg, first because the filtrate free from these flocks when heated with sugar gives a jelly. Secondly, this flocking body in currants is not present in other fruits. Thirdly, it differs from the pectin of von Fellenberg in not containing methoxyl groups. Lastly, when Tromp de Hass and Tollens analyzed this flocculating body, they found it evidently a carbohydrate containing 54.4 per cent carbon and 5.05 per cent hydrogen. It contains, therefore, a higher percentage of carbon than either cellulose or pectin.

To prove that pectin plays an important rôle in jelly formation von Fellenberg dissolved quince jelly in boiling water. From this mixture he precipitated pectin by adding alcohol. The filtrate would form only a syrupy solution, not jelly. If the precipitated pectin were added jelly formed. A similar result was obtained when purified pectin was added to quince syrup.

A purified pectin and sugar solution alone gave no jelly. Pectin from various fruits and varying quantities when added to a sugar solution resulted in syrups only. He concluded, therefore, that the formation of jelly is due to other substances than pectin and sugar.

If jelly formation be considered as a coagulation it might be supposed that a jelly would result by the addition of mineral salts which coagulate pectin to a solution of pectin and sugar. This was not the case, for when ferric chloride was added to a solution of pectin and sugar, flocks of a pectin-iron coagulum separated; no jelly formed.

Von Fellenberg obtained better results by using organic salts, i.e., malates of calcium, magnesium, and aluminum. These gave jellies when added to a solution of pectin and sugar. Such jellies were not as stiff as those formed by the addition of pectin to pectin-free fruit syrups. In summarizing his work with jellies, von Fellenberg concluded that besides sugar and pectin certain salts are necessary to jelly formation. He considered the possibility of other parts of fruit juice playing active rôles in jelly-making.

A previous investigator on jelly-making, Goldthwaite, noticed that jelly formation would occur when 0.5 per cent tartaric acid solution, 1 per cent pectin, and three-fourths volume of sugar were heated for not more than fifteen minutes. She considered the presence of free acid necessary for jelly. In fact she claimed that neutral juice would not gelatinize.

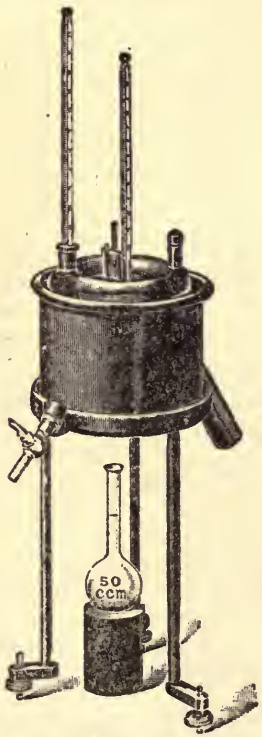
In considering earlier researches, I believe that the malates of calcium, magnesium, and aluminum may owe their virtue in gelatinization to the presence of the hydrogen ion. Acid malates may have been present as impurities in the salts used by von Fellenberg. It is doubtful if neutral malates would aid appreciably in gelatinization.[1]

In commencing work with pectin I considered the principal factors in securing jelly of proper consistency to be pectin, sugar, and acid.

[1]Tarr ("Fruit Jellies, No. 1, The Rôle of Acids," *Delaware Agricultural Experiment Station Bulletin*, No. 134, Tech. No. 2, 1923) has found that the minimum pH for jelly formation is 3.40, and that the pH for optimum jelly is 3.1.

The pectin used was obtained from Villa Franca and Eureka lemon rinds by the von Fellenberg process. Four kg. of lemon rinds were boiled in a reflux condenser six to eight times (twenty-minute periods) with 4–6 liters of 95 per cent alcohol. This process tended to free them from coloring matter, acids, etc. Between each boiling the material was pressed in a screw press. Three liters of water were added to the final press cake and the mixture heated in an autoclave for an hour at 110°C. At the end of this period the contents were pressed and the liquid was filtered through a Seitz asbestos filter until clear. The pectin was obtained from the filtrate by adding a double volume of alcohol to which 7 c.c. of concentrated hydrochloric acid had been added per liter. The coagulum was pressed in canton flannel and kneaded in several changes of alcohol until the acid reaction disappeared. Finally the pectin was washed with ether and dried in a vacuum desiccator over sulphuric acid.

The results show: (1) All three of the substances tested, when in aqueous solution, independently increase the viscosity of distilled water. (2) Mixtures of any two or all three of the substances result in an increase of viscosity greater than the viscosities independently. (3) Jelly will form when acid, pectin, and sugar are in solution of certain concentration. (4) Jelly will form from a solution of 3 gm. per cent pectin and 65 gm. per cent sugar. (5) The viscosities of the separate substances are not additive.



(A. H. Thomas Co.)

Fig. 12.—A Redwood viscosimeter.

According to Hardy and Robertson jelly formation is analogous in some instances to emulsification and may therefore be dependent on surface tension phenomena. From the Tolman theory of colloids in the case of a lyophylic colloid in equilibrium with a dispersing medium, an increase in the concentration of the hydrogen ion in the dispersing medium lessens surface tension and hence increases dispersion. Thus an increase in hydrogen ion concentration would result in an increase in the total surface of the pectin and consequently the viscosity of the solution could be increased. Still further additions of acid might lead to such high degrees of dispersion that the condition of affairs in so-called true solutions would be approached and thus the viscosity again decreased.[1]

The function of sugar may be that of a dehydrating agent. It also imparts a certain amount of viscosity to the jelly presumably by combining the water which would otherwise lead to fluidity. Glycerol acts similarly. The comparative anhydrous state of jelly may be shown by the addition of a small amount of either cupric chloride or cobalt chloride to the jelly. Green and red colors respectively result, which are the anhydrous col-

[1]See footnote 1, page 84.

ors of these salts. Upon dilution these colors change to blue and pink, the respective hydrous colors of the salts.

If the function of sugar is principally that of dehydration, then a higher concentration of pectin together with the same concentration of acid and no sugar should give a jelly of equal firmness to the one in which sugar is present. Indeed experimental results indicate such to be the case.[1]

In the viscosity experiments a Redwood viscosimeter was used. The results are tabulated in Table XIII.

TABLE XIII

VISCOSITY RESULTS ALL OBTAINED AT 45° C.

CITRIC ACID (BAKER'S ANALYZED) (GRAMS PER CENT)	CANE SUGAR (COMMERCIAL) (GRAMS PER CENT)	PECTIN (GRAMS PER CENT)	SPECIFIC GRAVITY	TIME OF FLOW			
				Trial I (min. sec.)	Trial II (min. sec.)	Trial III (min. sec.)	Average (min. sec.)
.....	65.0	.....	1.3204 at 23.5°	1, 59.2	1, 58.1	1, 54.3	1, 57.2
0.5	.....	.....	0.995	25.2	25.4	25.4	25.33
1.0	.....	.....	0.996	25.4	25.5	25.4	25.43
2.0	.....	.....	0.999	25.8	26.6	25.5	25.63
4.0	.....	.....	1.012	27.2	26.8	26.8	26.93
.....	.....	1.0	1.002	27.2	27.6	27.4	27.4
.....	.....	2.0	1.005	28.4	28.4	28.6	28.4
.....	.....	3.0	1.007	29.8	29.8	30.0	29.8
.....	.....	4.0	1.012	32.0	32.4	32.0	32.2
.....	65.0	1.0	.....	9, 10.4	9, 45.0	9, 31.0	9, 28.8
.....	65.0	2.0	.....	13, 25.4	13, 25.2	14, 00.0	13, 36.8
.....	65.0	3.0	.....	Jelly			
.....	65.0	4.0	.....	Jelly			
0.5	.....	1.0	.....	1, 10.0	1, 5.4	.....	.....
0.5	.....	2.0	.....	1, 22.4	1, 22.6	1, 22.0	1, 22.3
0.5	.....	3.0	.....	1, 18.8	1, 20.0	1, 21.6	1, 19.44
0.5	.....	4.0	.....	1, 22.8	1, 25.0	1, 22.0	1, 23.2
0.5	65.0	1.0	.....	Jelly			

SUMMARY

1. Pectin, acid, and sugar are the principal factors in fruit jelly-making.

2. Pectin was obtained from lemon rinds by boiling in several changes of alcohol, heating in an autoclave for one hour at 110°C. in

[1]Confirmatory evidence toward the functioning of sugar as a dehydrating agent has been obtained by Holmes and by Tarr and Baker ("Fruit Jellies, No. 2, The Rôle of Sugar," *Delaware Agricultural Experiment Station Bulletin*, No. 136, Tech. No. 3, 1924. H. N. Holmes and H. A. Howe, "The Rôle of Pectin in Gel Formation," *Science*, New Ser. LVIII [1923], 314).

the presence of water, filtering precipitating by a double volume of acidified alcohol, removal of acidity with alcohol and ether, and finally drying in vacuum desiccator over sulphuric acid.[1]

3. The results of the viscosity experiments indicate that: (*a*) Pectin, acid, and sugar independently or combined increase the viscosity of water. (*b*) Jelly will form from a mixture of acid, pectin, and sugar when in certain concentration. (*c*) Jelly will form when pectin and sugar are dissolved in certain concentration. (*d*) The viscosities of the various substances are not additive. (*e*) The increase of viscosity may be due to the presence of the hydrogen ion. (*f*) That sugar may have two functions, viz., that of a dehydrating agent and of increasing the viscosity.

THE PRODUCTION AND USES OF PECTIN

PECTIN EXTRACTION[2]

Boyles of the Washington State University has perfected a process and patented the methods of extracting pectin from apples and oranges. The pectin is extracted with hot water and then precipitated from solution by the addition of alcohol. The alcohol is then evaporated and impure pectin remains.

It has been shown by Bigelow, Gore, and Howard that six hours' boiling with water under a reflux condenser, with changes of water at the end of every hour, does not completely remove all pectin from apple pulp previously freed of sugars and other materials soluble in cold water, alcohol, or ether. (Pectin solution can be greatly accelerated by heating under pressure in an autoclave.) The pectin is thus dissolved in a very large volume of water, and the problem to be solved is the reduction of this dilute solution to a small volume. Pectin cannot be prepared by evaporating a dilute solution in water unless the work is carried on in a partial vacuum at a low temperature, since long-continued boiling brings about chemical changes which involve the loss of gelatinizing properties. It could be precipitated from such solutions by the addition of alcohol, but precipitation does not occur until the

[1]Singh ("Practical Experiments in Jelly Making," *Journal of Industrial and Engineering Chemistry,* XIV [1922], 710) has carried on confirmatory experiments.

Sucharipa ("Experimental Data on Pectin-Sugar-Acid Gels," *Journal of American Official Agricultural Chemists,* VII [1923], 57–68) consider jelly formation to be due to the coagulation of pectin in the liquid sugar-acid medium, there being no chemical reaction involved. Pectin is described as being very slightly soluble in sugar-acid solutions of certain concentrations.

[2]United States patents involving pectin manufacture are: R. Douglas, No. 1082682, December 30, 1913; R. Douglas, No. 1235666, August 7, 1917 (pectin solution); R. D. O. McDill, No. 1365000, January 11, 1921.

percentage of alcohol in the mixture has reached 51 per cent. This would necessitate the use of large quantities of alcohol, impossible to recover except by repeated distillation, and would be entirely too expensive for general use.

The method employed by Caldwell for securing concentrated solutions of pectin was suggested by Gore's method for concentrating fruit juices. This method consists essentially in separation of a portion of the water of the juice by freezing, removal of the concentrated liquid from the ice by centrifuging with repetition of this process until the desired concentration has been attained. The following description of a typical experiment will make the method clear:

Twenty kilos (44 lb.) of mature Winesap culls were ground to a fine pulp in a small meat chopper, placed in a graniteware vessel, enough cold water (3,000 c.c.) added to cover them, and slowly heated to boiling. After two hours of gentle simmering the whole was placed in a double muslin bag and suspended over a vessel to drain. When dripping had entirely ceased the pulp was returned to the cooker, 2,500 c.c. cold water added, and again slowly cooked. Four successive cookings of approximately two hours each extracted the pectin so completely that the extract no longer gave an appreciable precipitate of pectin when allowed to fall drop by drop into strong alcohol. The pulp was then gently pressed to extract as much liquid as could be forced out without forcing fragments of pulp through the muslin, and the various extracts were collected and measured. During the cooking 12,000 c.c. of water had been added and the total quantity of extract measured 23,456 c.c. (24.8 qt.).

This liquid was now placed in tall, enamel-lined tin cans and subjected to freezing by exposing it on a window-sill over night, at a temperature of 15°–20°F. The cans were filled next morning by a mass of knifeblade-like platelets and spicules of pure water ice, holding between them a quantity of liquid containing all the solids of the extract. The cans were emptied into a large graniteware vessel, the ice was crushed by the use of a wooden mallet, and the liquid separated from the ice in an ordinary cream separator turned slightly faster than for separating cream. Five minutes sufficed to separate the liquid completely from a charge of ice. This treatment reduced the original 23,456 c.c. to 9,308 c.c., which was returned to the cans, again frozen and separated, yielding 5,626 c.c. A third and a fourth freezing and separation reduced the volume to 2,260 c.c. The liquid was now of a very dark-brown color and of the consistency of a thick syrup, as it contained not only the pectin, but also the sugar and the coloring matter of the entire extract. (The nitrogenous constituents had been coagulated by the long heating to which the fruit had been subjected, and hence did not pass into the extract.)

The extract was now further concentrated by placing it upon a shelf at such a distance above a radiator that it would be kept at a temperature of 158°F. Here it remained four days, becoming reduced to 1,509 c.c. or less than one-fifteenth its original volume, when solidification at the surface practically stopped further loss of water. The extract was now

treated by the Goldthwaite method for precipitating pectin. The mass was slowly poured from a beaker into a vessel containing 1,600 c.c. of 95 per cent alcohol, which caused precipitation of the pectin as a gelatinous, rubber-like mass, the sugars and coloring matter for the most part remaining in the alcohol. The mass of pectin was collected on a cheesecloth filter, the alcohol worked out of it with a spatula, and it was then washed with previously filtered alcohol which had been used in the precipitation, followed by small quantities of fresh alcohol. To further purify it, it was now dissolved in 1,000 c.c. of lukewarm water, which required occasional stirring for several hours to secure complete solution, and reprecipitated by pouring into 1,000 c.c. of 95 per cent alcohol, after which the alcohol was pressed out with a spatula. The mass of pectin was then dried slowly at a temperature of 158°F. The dry pectin is a whitish gray mass easily ground into a grayish powder which dissolves readily in warm water, and has not undergone change upon keeping in a corked bottle on the laboratory shelf for more than five months. A good jelly was made by adding 1 per cent by weight of this powder to water in which ½ per cent tartaric acid had previously been dissolved, adding 65 per cent by weight of sugar, and boiling for fifteen minutes.

It occurred to Caldwell that if the activity of the concentrated extract were reduced to such a point that the pectin would not be affected thereby, it should be possible to keep such a preparation for a long period without deterioration, as the very high content of sugar and the absence of nitrogenous material makes such an extract a very unfavorable medium for the growth of fungi. This hypothesis was tested out in the following way: 12,000 c.c. of water extract made from 10 kilos of Ben Davis culls was reduced by two successive freezings to 4,763 c.c. The liquid was transferred to a tall vessel and 12 gm. powdered lime carbonate (precipitated chalk) was slowly added with constant stirring. Lime carbonate reacts with the malic acid of the juice to form an insoluble salt, calcium malate. As soon as the addition of the carbonate had been made, the liquid was thoroughly stirred and divided into two equal parts in order that two methods of removing the calcium malate might be tested.

One lot was immediately transferred to a graniteware vessel, brought to a boil, and filtered through filter paper while boiling. Filtration was effective in removing the calcium salt but was rather slow.

The second lot of extract was allowed to stand undisturbed for twelve hours after the addition of the lime carbonate. At the end of that time the calcium malate formed had collected at the bottom and upon the sides of the vessel as a thin, granular precipitate. The clear liquid could be siphoned off without disturbing this precipitate, and it was also possible to decant without the loss of more than a few c.c.

The two portions of extract, after precipitation and separation of their acid as the calcium salt, consisted of 2,365 c.c. each. They were kept separate, reduced to 725 and 743 c.c. respectively by two successive freezings, then transferred to beakers and reduced by slow evaporation over a radiator at 70°C. to a volume of 400 c.c. each. They now had the consistency and the color of tomato catsup. Two grapejuice bottles were sterilized by thorough boiling and the contents of the two beakers were transferred

to them and sealed. "These bottles have been kept upon an open laboratory shelf for four and one-half months, have been twice opened and resealed after removal of a part of the contents, and are at the present time free from evidence of growth of bacteria or fungi, while the pectin retains its power of causing gelatinization without decrease." Preparations made without removal of the acid slowly lose their power to cause gelatinization, losing somewhat more than half their efficiency in the first three weeks after preparation. Preparations of dry pectin made by precipitating with alcohol and drying at a low temperature undergo no discoverable change in their efficiency when kept in sealed bottles for months.

The concentrated pectin solution made by freezing and evaporating is, of course, very far from pure, since it contains not only the sugars present in the fruit used but also the coloring matters and such flavoring substances as were not volatilized by heat. However, its addition to any fruit juice will not produce greater change in color and flavor than would be produced by the addition of an equivalent volume of apples. The powdered pectin, on the other hand, is practically free from coloring matter, has no discoverable apple odor or taste, and will not cause deterioration in flavor of even the most delicate jellies, to which its use may well be restricted because of the greater labor and cost of preparation.

Caldwell later developed a method for preparing pectin by the use of ammonium sulphate as a precipitant. The principle of this method is based upon the fact that pectin as extracted from the pulp or pomace is in a colloidal state and can be readily changed by electrolytes. Since pectin, after precipitation, must be dispersed again in order to be of any value as a gelatininzing agent, an electrolyte that will produce a reversible precipitation must be chosen. Also the electrolyte chosen must be non-poisonous. Lead acetate will precipitate pectin, but the precipitation is an irreversible one, and the amount of lead absorbed or combined may be poisonous. For these reasons ammonium sulphate was selected. Bourquelot and Hérissey used ammonium sulphate as a precipitant for pectin obtained from gentian root.

Sixty gm. of dried apple pomace were boiled three successive times with 200 c.c. of water, filtering after each boiling. To each of the 100 c.c. of filtrate 25 gm. of ammonium sulphate were added[1] and then heated to 70°C., whereupon the pectin was precipitated as a grayish-white flocculent precipitate. The precipitate was separated from the mother-liquor by filtering. (The mother-liquor can be evaporated and the residue used again or the residue can be used as a fertilizer.) The precipitate was dissolved in hot water and again precipitated with ammonium sulphate. Again it was filtered and the precipitate was removed from filter paper and dried at 60°–70°C. and when dry was washed several times with cold water to remove adhering ammonium sulphate. The precipitate was dried again and its gelatinizing power was tested by adding to a 1 per cent solution of the pectin, 0.5 per cent solution of citric acid, and 65 gm. of sugar. This

[1]If wet pomace is used it will require a somewhat larger amount of ammonium sulphate. First add 25 gm. per 100 c.c. and if precipitation does not occur, add successive portions of 5 gm. until precipitation occurs. The pectin may also be precipitated by saturating the solution in the cold with ammonium sulphate.

solution was boiled for ten to twenty minutes and upon cooling a jelly was produced. The taste did not indicate the presence of ammonium sulphate and upon dissolving the jelly in hot water only a slight milkiness was produced when tested for sulphates.

In order to determine whether the yield of pectin by the foregoing method was equal to the yield produced by the alcohol precipitation method, two samples of apple pomace from the same lot were treated exactly alike, except that ammonium sulphate was used in one case and alcohol in the other as the precipitating medium. The pectin was dissolved and reprecipitated in each case, then filtered, and the precipitate was removed from filter paper and dried. The ammonium sulphate was removed from the one by washing with cold water, again dried and weighed. The amount of pectin recovered by each method is recorded in Table XIV below.

TABLE XIV

Precipitant	Pectin Per Cent
Ammonium sulphate	6.33
Alcohol	6.91

The amount of ammonium sulphate used can be reduced by concentrating the extract, either by evaporating on a steam bath, in a partial vacuum, or by freezing. The quality of the pectin is not impaired in either case.

It has been found quite difficult, however, to free the final pectin obtained by this method from ammonium sulphate.

METHODS FOR PECTIN ESTIMATION

Perhaps the method most generally used at present is simply that of precipitation from aqueous solution by alcohol, filtering, washing with alcohol and ether, and drying in a desiccator over sulphuric acid. This, however, requires a long time and is not absolutely accurate owing to impurities and to the deliquescence of pectin.

If the pectin solution is free from impurities the amount of pectin may be obtained by determining the viscosity of the solution, as shown by McNair (p. 92).

T. B. Robertson suggested to the writer that a method might be evolved for the determination of pectin through use of its refractive index. The refractive index of a 2 per cent water solution of lemon pectin was found to be 0.00130 per gm. per cent when observed in a Pulfrich refractometer which indicates to within 1′ of the angle of total reflection. A sodium flame was employed as a source of light. The solution was adjusted to the temperature of the room so that the temperature of the refractometer prism and that of the solution used would be the same. It has been shown by Robertson that in alkaline or acid aqueous solutions of proteins the change in the refractive index of the solvent is directly proportional to the concentration of the dissolved protein. In respect to its refractive index pectin acts similarly to protein. This relation can be expressed by the equation:

$$n - n_1 = a \times c$$

when n is the observed refractive index of the pectin solution, n_1 that of the solvent in which the pectin is dissolved, c the percentage of pectin in solution, and a a constant, expressing the change in the refractive index of the solvent by the addition of 1 gm. of pectin per 100 c.c. In using this method the refractive indices of impurities would also have to be determined.

For most purposes the estimation of pectin through its methyl alcohol content may be most satisfactory. This can be done as outlined on pages 80–81 by making use of either Zeisel's or Denigès method for methoxyl estimation.

JELLY MANUFACTURE[1]

To produce a jelly of the proper consistency, the fruit used must contain a good supply both of pectin and acid, or if not a large supply of pectin, a large amount of compounds that break down into pectin at the temperature of boiling water. Some fruits were found by Cruess and McNair to contain a sufficiency of acid and pectin while others lacked one or the other of these necessary constituents. Where the fruits were low in acid, attempts were made to produce jelly without addition of acid and also with addition of citric acid or lemon juice. In most cases the pectin was extracted in the usual way by cutting the fruit into small pieces, adding water to cover, boiling slowly until tender and expressing the hot juice by pressing in a small fruit press or by straining through a coarse cloth with gentle pressure.

The solution so obtained was analyzed for Balling or Brix degree (percentage of dissolved solids) and acidity, and, if much more dilute than the juice of the fresh fruit itself, was concentrated before being made into jelly. In making jelly, sugar was added in most cases at the rate of one and one-quarter volumes of sugar to one of solution. The mixture was then heated to boiling and boiled down to a boiling point of 104°–105°C., or to a concentration of 65–70 per cent dissolved solids. At these concentrations, a jelly will form if the fruit is suited to the purpose.

Yields.—The amount of jelly obtainable from any fruit without addition of acid will depend on the pectin and acid content of that fruit. Maximum yields from several fruits were obtained by making from four to six successive extractions of pectin by boiling the fruit with water and pressing. The several extracts were kept separate and tested individually for their jelly-making properties. They were also combined in various amounts to ascertain the maximum amounts of pectin solutions from the last extractions that could be blended with the first two extracts and still give a jelly. Oranges and lemons mixed in the ratio of two oranges to one lemon gave a maximum yield of 1,585 c.c. jelly per 1,000 gm. of fruit, or approximately 392 gal. of jelly per ton of fruit, or 8,363 6-oz. glasses of jelly per ton. Yields of 300 gal. of jelly from the mixed fruits have been obtained often in the laboratory. Red loganberries gave a maximum yield of

[1]United States patents involving jelly manufacture are: F. L. Jefferies, No. 1045849, December 3, 1912; P. R. Boyles, No. 1067714, July 15, 1913 (jelly base, pectin and acid mixed); R. Douglas, No. 1304166, May 20, 1919; M. O. Johnson, No. 1362869, December 21, 1920 (concentrated jelly); R. D. O. McDill, No. 1365001, January 11, 1921 (dried jelly).

1,890 c.c. jelly per 1,000 gm. fruit or approximately 467 gal., or 9,962 6-oz. glasses per ton. Similarly, Mammoth blackberries gave 290 gal. jelly per ton. With addition of acid, these yields were considerably increased so that the yields were limited rather by lack of acid than lack of pectin.

Clarification.—A jelly to be most attractive should be clear. Two methods of clarification are in general commercial use. The most common practice is to filter the hot pectin solution. Often the boiled fruit and liquid are thrown together into some form of cloth or felt bag filter. This process is slow and troublesome and does not ordinarily give a brilliantly clear filtrate.

The second method consists in sterilizing the hot juice from the press in 5-gal. cans. These are stored until the sediment deposits. This will ordinarily be a period of several months. The settled juice is then decanted or siphoned off from the sediment directly into the cooking kettles. The process is often modified to the extent of giving the hot juice a bag filtration before canning.

Laboratory tests were made to ascertain the effect of Spanish clay and infusorial earth on the rate of filtration. These substances were added in powdered form to the hot juices and the rates of filtration and clearness of filtrates compared with those of the untreated juice. The Spanish clay, when added dry, gave an "earthy" taste and did not appreciably hasten filtration. Infusorial earth, when added at the rate of 5 gm. per 100 c.c., greatly increased the rate of filtration and gave a clearer filtrate with one filtration than could be obtained without the addition of this substance. It was also found that the filtration through short fiber asbestos pulp in the Seitz type of filter was very much more rapid and resulted in a clearer filtrate than was obtained with the bag filter. A mixture of Seitz asbestos No. 5 and Seitz "Brilliant" asbestos added to and mixed with the juice to give a filtering layer about ⅜ in. thick gave good results. The flavor of the juice is not impaired. Filtration in all cases is made before any sugar is added to the juice.

Jelly stocks from loganberries, currants, and a mixture of oranges and lemons were prepared by boiling the fruits with a small amount of water until soft and pressing through a coarse cloth. The oranges and lemons were mixed in the ratio of two oranges to one lemon before boiling. The juices were divided into small portions. To these portions were added casein from a 2 per cent solution in dilute NH_4OH at the rate of 20, 40, 60, and 100 gm. per hectoliter, respectively. To other portions were added egg albumen in the same amounts as noted for casein. To others were added 250, 500, 1,000, 1,500, and 2,000 gm. of Spanish clay per hectoliter from a 10 per cent suspension of this substance in water. Untreated checks were also prepared. The various lots were bottled and sterilized one-half an hour at 100°C. It was found that the lemon-orange jelly stock settled very satisfactorily in twenty-four hours after sterilization without the addition of any clarifying material. The untreated loganberry and currant checks did not settle very satisfactorily in twenty-four hours, but after several weeks' storage did settle fairly well. Currant juice prepared by heating the crushed fruit to 85°C., pressing and sterilizing at 85°C., settled better

than the juice from the same fruit heated to 100°C. The casein and egg-albumen findings gave poor results in all cases and resulted in making the liquids more cloudy than the untreated checks. Spanish clay at 250 gm. per hectoliter did not aid in clearing; 500 gm. per hectoliter seemed to aid considerably in clearing. In some cases, 1,000 gm. per hectoliter gave a perfect clarification in twenty-four hours; in other cases, 1,500 to 2,000 gm. of Spanish clay per hectoliter were needed to effect clearing of the juice. This was especially true of loganberry juice. In applying this method in practice, preliminary tests on a few hundred c.c. of the material should be made before clarifying any large amount.

The Spanish clay was prepared by soaking it in a small amount of water into a finely divided, thin "mud" or suspension. This can be made to a definite concentration, e.g., 20 per cent or 10 per cent mixtures were found satisfactory. The flavor of the juice is not impaired by the use of the clay in this form.

Preliminary tests with fire clay indicate that this substance can probably be used in a way similar to that employed with Spanish clay.

Aroma and flavor changes in jelly-making.—Fruit jellies when made in the ordinary way usually differ in aroma and flavor from the fresh fruits from which they are made. Ordinarily, jellies are made by extracting the pectin by boiling, followed by addition of sugar and boiling until the mixture boils at about 220°F., or until the mixture jells, or until a Balling or Brix degree of 65 (corrected for temperature) is obtained. The high temperatures result in marked changes in flavor, and give a so-called "cooked" taste to the product. Experiments have proved that the usual high temperature of the second boiling is not required in all cases and that the fruit flavor may then be retained.

It was thought that this change in flavor and aroma might be due in part to hydrolysis and in part to loss by volatilization. To throw light on loss by evaporation, attempts were made to make jelly from currants, loganberries, blackberries, and a mixture of orange and lemons, at temperatures of room temperature, 60°, 70°, 80°, 90°, and 100°C. The fruits were crushed and heated in water-jacketed aluminum pots to the temperatures indicated and pressed. Cane sugar was added to increase the Brix degree to 65 and to dissolve the sugar the juices were heated to the respective temperatures indicated.

To note whether loss of flavor was also due to hydrolysis, a second series at the same temperatures indicated above was carried out in a 500-c.c. flask fitted with a long water-cooled reflux condenser.

The jellies made by the two methods were compared shortly after they were made. The jellies made in the open kettle at the lower temperatures were superior to those made at the higher temperatures as regards amount of fresh fruit flavor and aroma retained. The same applied to the jellies made under the reflux condenser. After two to three months' storage, the differences in flavor and aroma were not so pronounced. The orange jelly, after long storage, developed a "turpentine"-like taste, probably due to oxidation of the orange oil.

The jellies made at room temperature by the addition of sufficient sugar (to 65° Brix) and citric acid (to a total of ½ per cent) to jelly

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stocks were especially close to the flavor of the fresh fruits from which they were made. Loganberry and in one or two cases blackberry and orange jelly were thus made without application of heat, but strawberries did not yield a jelly in any case. Loganberries very readily give a highly flavored aromatic and firm jelly in this way. So far as known, this method has not been described before.

The facts that jellies made at high temperatures (85°–105°C.) were poorer in fresh fruit flavor than those made at room temperature and 60°–75°C., and that jellies made under the reflux condenser were stronger in fresh fruit aroma and flavor than jellies made at the same temperatures in an open kettle, indicate that loss of flavor and aroma is due both to volatilization and to decomposition of flavoring and aromatic bodies.

Sugar in jelly-making.—The addition of sugar in jelly-making is necessary to raise the concentration of dissolved solids sufficiently to cause the formation of a gel with the pectin. The amount of sugar necessary will depend upon the pectin and acid concentrations, but the amount used normally is controlled by the concentration of sugar necessary to prevent fermentation or molding. Tests with loganberry and orange jellies showed that jellies could be obtained at 60° Brix or lower, but that in such cases molding or fermentation took place unless the jellies were sterilized in sealed containers. Jellies with varying amounts of sugar were inoculated with mold and yeast and caps were placed on the glasses. It was found that 65° Brix prevented spoilage, but that much below this concentration mold growth took place. Where the sugar concentration was increased from 72° to 75° Brix crystallization of sugar often took place. This crystallization depends on the amount of cane sugar present. The tendency to crystallize was most noticeable in jellies of low acid content and in which little hydrolysis of the cane sugar had probably taken place. Where glucose is used for jelly-making, the concentration may be considerably above 70° Brix without crystallization.

A simple method for calculating the amount of sugar to add to a juice of a given degree Brix to bring the liquid to 65° Brix is as follows:[1]

Let a = Brix of juice.
V = Volume of juice.
S = Grams sugar necessary to bring to 65° Brix.
Then $(65 - a)V/35 = S$.
Example:
$V = 250$ c.c. $\quad a = 5$ Brix.
$(65 - 5)\ 250/35 - S = 428.5$ gm. sugar.

For practical purposes, a little more than one and one-half of sugar to one of juice by weight will be found satisfactory.

If this method is used, the fruit juice cannot be so dilute as where a mixture of one of sugar to one of juice is used and where the pectin is concentrated by boiling off excess water. The juice must contain enough

[1]A more exact formula is $y = 1.4x + 0.002512x^3$ where x = degrees Brix of syrup and y = the ounces of sugar added per gallon of water at 17°C. (J. B. McNair, "Syrups for Canning and Preserving," *Journal Industrial and Engineering Chemistry*, IX [1917], 151).

pectin to give a jelly without concentration of the juice after addition of sugar.

Sugar added to the crushed fruit before pectin extraction seemed to help retain the flavor and the jelly so made appeared to be superior in this respect to jelly made by the usual methods.

A solution of 65° Brix will boil at 103.9°C. or 219.02°F. at sea-level. This point can be used to determine the proper density of the boiling jelly if the proper allowance is made for elevation of locality in which the jelly is made. The boiling-point of water for any given locality may be determined and then the boiling-point of jelly at the proper concentration will be 3.9°C. or 7.02°F. above the boiling-point of water.

Acid in jelly-making.—It was found that pectin solutions made by boiling and pressing fruit and containing less than 0.5 per cent acid (as citric or tartaric) usually did not jell, but it was also found that if the acid were increased to 0.7 or 0.8 in such cases, it almost invariably gave a jelly. This was noticed especially with citron melon and fig solutions, both naturally deficient in acid, but containing sufficient pectin for jelly-making. Tests made with a 1 per cent solution of pure orange pectin in distilled water indicated that a concentration of 0.3 per cent acid in the final jelly was necessary to give a firm jelly. Increase of acid in the final jelly to 1.9 per cent acid resulted in softening of the jelly; 1 per cent acid in the final jelly gave good results and corresponds to about 1.5 acid in a fruit juice before addition of sugar; 0.3 per cent acid in the final jelly would similarly correspond to about 0.5 per cent acid in the fruit juice before addition of sugar. This would indicate a range of 0.5 to 1.5 per cent acid in the original fruit juice for the proper concentration of acid calculated as citric acid. This corresponds very well with results obtained with pectin-containing orange juices made by boiling this fruit and pressing. In this case an acidity of 1.5 per cent in the juice gave a finished jelly that set quickly but which finally softened, while 0.5 per cent gave a fairly good jelly, and less than 0.5 per cent did not give a jelly or resulted in a very soft jelly.

Working with purified pectin and different amounts of pure citric acid, it was found that for the same treatment as regards amounts of sugar added, time of boiling, etc., the color of the resulting jelly was darkened in direct proportion to the amount of acid used. The colors were compared by means of a Dubosq colorimeter. This darkening is probably due to caramelization of the sugar.

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CHAPTER IV

OTHER PRODUCTS FROM THE RIND

The rinds of the orange, lemon, and citron are made into articles of commerce by candying or drying.

For this purpose the peel is separated from the fruit either by hand or machine[1] and is dried either by laying it in trays in the sun, as in fruit drying, or by a current of heated air. Market for this product is found with wholesale druggists, although some is sold for use in dried mince meat and similar preparations. Candied peel is made somewhat similar to glacéd fruit.

Glacéd kumquats are prepared in China and Japan. The fruit is picked when ripe and several slits are made in the sides, sometimes the seeds are squeezed out through the slits, sometimes not. The fruit is next boiled until tender and then placed in a dilute sugar solution. From this it is soaked in a series of sugar solutions of gradually increasing density. They are next dried and then dipped into a very hot syrup and again dried. The final product has the sugar glacéd on the surface of the fruit (Coit). Glacéd kumquats acquire an unattractive "turpentine" taste in time, due to the decomposition of the rind oil.

Some of the candied citron of commerce is prepared where the fruit is grown, chiefly in Mediterranean localities, the principal production centering in Leghorn, Italy, and in Corsica, but far the greater proportion of candied citron is in recent years manufactured in England or in the United States, the Corsican or Italian fruit being imported preserved in brine.

The fruit is simply cut in halves, the seeds scooped out, and without peeling the fruit is thrown into brine, cooped up, and shipped in casks. Though either green or ripe fruit may be used, the demand is mostly for fruit having a green color and therefore the green fruit is preferred.

[1]One of the most successful types of machines used consists of an axle to which is attached in the middle a steel pulley 3 or 4 in. in diameter, and on each end a conical bur. The axle passes through the centers of the bottoms of two aluminum tea kettles each of which surrounds a bur. The spouts of these kettles are turned toward the floor and serve as exits for the juice. In operating the machine the burs revolve about 1,000 times per minute, and a half of a fruit is held against each bur. The burs are frequently made of apple wood although often of bronze. The machine requires about one-half a horse-power to operate. An experienced man can handle one lug box (60 lb.) of lemons in twelve minutes or twenty-five boxes in eight hours. If the capacity of the machine be considered from the standpoint of the juice secured, it can make 35 gallons of lemon juice in one hour.

The candying process involves boiling in water to remove the salt and soften the fruit which is then immersed in cold water to intensify its green color. It is next covered with hot syrup and allowed to stand three or four weeks, during which time the strength of the syrup is gradually increased or in practice the fruit is transferred from tank to tank with a gradually increasing sugar concentration and the fruit boiled with syrup, cooled, more sugar added, and again boiled until no more sugar is taken up. The pieces of fruit are then dried, coated with white sugar crystals, wrapped in tissue paper, and packed in wooden boxes.

The annual consumption in the United States averages about 4,000,000 lbs.

In Dominica a small business is done in shipping limes pickles in sea-water. These limes go chiefly to Boston. The trade is only a small one, and during late years the export of pickled limes has fallen off somewhat. This is probably not due to a decreasing demand for pickled limes, but rather to increasing shipments of this product from other

TABLE XIII A

IMPORTS OF CITRON OR CITRON PEEL INTO THE UNITED STATES
1898–1923

YEAR ENDING JUNE 30	DRIED, PRESERVED OR CANDIED		IN BRINE		TOTAL	
	Quantity (Lb.)	Value	Quantity (Lb.)	Value	Quantity (Lb.)	Value
1898	81,866	$ 6,032.00	.....	.....	81,866	$ 6,032.00
1899	54,400	3,411.00	.....	.....	54,400	3,411.00
1900	113,141	7,211.00	.....	.....	113,141	7,211.00
1901	104,012	6,862.00	.....	.....	104,012	6,862.00
1902	162,561	11,439.88	.....	.....	162,561	11,439.88
1903	742,045	43,815.00	.....	.....	742,045	43,815.00
1904	534,336	38,632.00	.....	.....	534,336	38,632.00
1905	311,436	26,105.00	.....	.....	311,436	26,105.00
1906	375,112	33,743.00	3,307,338	$165,531	3,682,451	199,274.00
1907	646,440	69,286.00	1,348,161	127,432	1,994,601	196,718.00
1908	1,020,506	94,391.00	3,518,419	188,457	4,588,925	282,848.00
1909	991,341	75,519.00	4,075,835	100,224	5,067,176	179,743.00
1910	773,736	56,960.00	3,431,601	122,239	4,205,337	179,199.00
1911	880,876	60,770.39	3,977,189	122,620	4,858,065	183,390.00
1912	881,644	57,217.50	2,786,075	141,559	3,667,719	198,778.00
1913	515,686	41,218.63	1,773,187	63,771	2,288,873	104,990.00
1914	849,557	66,849.00	2,482,940	106,677	3,332,497	173,526.00
1915	1,386,564	113,262.00	2,866,982	87,127	4,253,546	200,389.00
1916	1,067,127	97,916.00	3,856,253	141,804	4,923,380	239,720.00
1917	571,053	73,415.00	3,161,691	165,866	3,732,744	239,281.00
1918	467,574	89,583.00	3,112,322	175,389	3,579,896	264,972.00
1919	368,952	77,830.00	1,961,985	193,798	2,330,937	271,628.00
1920	559,520	174,545.00	4,013,740	614,255	4,573,260	788,800.00
1921	639,231	234,114.00	2,330,544	267,331	2,969,775	501,445.00
1922	1,144,763	253,423.00	3,376,260	356,646	4,521,523	610,069.00
1923	1,701,619	460,171.00	1,931,434	245,669	3,633,053	705,840.00

TABLE XIII B

IMPORTS OF ORANGE AND LEMON PEEL INTO THE UNITED STATES
1898–1923

YEAR ENDING JUNE 30	PRESERVED OR CANDIED		NOT PRESERVED OR CANDIED		TOTAL VALUE
	Quantity (Lb.)	Value	Quantity (Lb.)	Value	
1898.....	66,124	$2,576.44	.....	$5,309.57	$ 7,886.01
1899.....	139,633	2,934.39	.....	12,890.98	15,825.37
1900.....	126,036	3,887.00	.....	5,804.80	9,691.80
1901.....	208,680	4,795.56	.....	5,564.00	10,359.56
1902.....	436,791	9,361.68	.....	4,893.00	14,245.68
1903.....	165,003	8,086.00	.....	4,075.00	12,161.00
1904.....	236,293	11,433.96	.....	31,891.00	43,324.96
1905.....	225,280	10,611.17	.....	4,547.00	15,158.17
1906.....	224,613	13,027.00	.....	4,237.00	17,264.00
1907.....	470,052	26,949.00	.....	8,206.00	35,155.00
1908.....	613,834	40,342.00	.....	3,762.00	44,104.00
1909.....	436,129	20,692.98	.....	4,833.00	25,525.98
1910.....	643,114	32,066.94	.....	11,606.00	43,672.94
1911.....	700,900	34,883.24	.....	5,130.00	40,013.24
1912.....	464,213	24,275.50	.....	5,765.00	30,040.50
1913.....	654,307	34,435.00	.....	18,451.00	52,886.00
1914.....	563,666	34,004.00	.....	24,372.00	58,376.00
1915.....	541,833	29,323.00	.....	13,301.00	42,624.00
1916.....	411,109	29,207.00	.....	8,541.00	37,748.00
1917.....	200,390	18,446.00	.....	17,726.00	36,172.00
1918.....	181,164	19,667.00	.....	21,425.00	41,092.00
1919.....	123,355	18,797.00	1,122,388	43,542.00	62,339.00
1920.....	160,411	27,185.00	950,504	60,404.00	87,589.00
1921.....	378,392	72,110.00	464,983	19,822.00	91,932.00
1922.....	339,883	49,250.00	476,070	10,730.00	59,980.00
1923.....	688,274	88,196.00	1,799,589	42,850.00	131,046.00

West India islands. The average annual export of pickled limes from Dominica for the five-year period ending 1896, was 1,505 casks, for a similar period ending 1901, 1,117 casks, and for five years ending 1906, 1,000 casks. A cask holds about 2,000 limes.

For pickling, the finest specimens of sound yellow limes are selected and placed in vats into which sea-water is pumped in two or three days, this water is run off and fresh sea-water pumped in. This process is repeated several times until the limes are cured. The fruit is then placed in casks which are in turn filled with sea-water to which a small amount of salt has been added. The casks are then closed, and are ready for export.

CHAPTER V

PRODUCTS FROM THE PULP[1]

The pulp of citrus fruit serves for a variety of products. That of oranges and grapefruit is preserved by canning; the juice of these as well as of limes is extracted and bottled as such, or mixed with other fruit juices, or concentrated; citrus juice, particularly that of oranges, is converted by fermentation into wine, alcohol, vinegar, or acetone; citric acid is manufactured from the juice of lemons and limes.

CANNED PEELED FRUIT

Owing to higher cost and poorer flavor canned citrus fruit cannot compete directly with fresh, but it is acceptable both in flavor and appearance. It serves to supply vessels taking long voyages, mining, lumber and construction camps, and other inaccessible places. In California the orange canning season for navel oranges ranges between February and June, and for Valencia oranges between May and September. The season for canning grapefruit in Florida naturally coincides with height of the shipping season there. Fruit canned when immature becomes bitter and poor in flavor; on the other hand, fully ripe oranges having a good full flavor are sometimes lacking in acidity. This deficiency is remedied by the addition of lemon juice.

Oranges for canning are peeled by cutting the rind around the center, dropping in hot water to separate skin from pulp, and slipping the peels off by hand. They are next sliced and placed for a certain time in a definite strength of cane sugar syrup to impregnate the fruit with syrup. They are then placed in cans, covered with a 32 per cent syrup, exhausted, capped, and sterilized at a moderate temperature.

It should be noted that oranges when heated above 185°F. have their flavor greatly spoiled. The orange oil should not enter the product as it decomposes, producing what is called a "turpentine" taste. Sterilization is accomplished by heating the fruit for three hours at 120°F. or for twenty minutes at 145°–155°F.

[1]United States patents pertaining to the use of pulp are: D. F. Sherman, No. 744810, November 24, 1903 (dried with binder); D. F. Sherman, No. 793615, June 27, 1905 (dried by heat); H. A. Shepard, No. 1257410, February 26, 1918 (concentrated pulp by heat); D. F. Sherman, No. 793614, June 27, 1905 (dried by heat); P. R. Welch, No. 1277672, September 3, 1918 (preserved by heat); R. D. O. McDill, No. 1361079, December 7, 1920 (concentrated pulp paste with addition of sugar).

JUICES, PRESERVED[1] AND CONDENSED

Orange juice apparently satisfies the average taste best when it contains eight parts of sugar to one of acid and, therefore, must be secured when the fruit is fully ripe. Bitterness must also be guarded against; oranges from the middle of the season until its end do not give bitter juice. Lemon, grapefruit, and lime juices also vary according to their degree of ripeness. They, too, are liable to become bitter.

None of these fruit juices will ordinarily retain their natural flavors longer than twelve hours and many methods for their preservation have been undertaken. It is a comparatively easy matter to clarify these juices, bottle, and preserve them against fungus attack, but such products have not the color, flavor, or aroma of fresh juice. In attempting to find a suitable method for preservation many procedures have been tried, e.g., pasteurization, sterilization by heat, ozone, sulphurous acid, carbon dioxide, fluorides, benzoates, and the ultra-violet rays, together with the addition of sugar or partial fermentation.

One of the chief defects so far insurmountable in this line has been a "limey" or "musty" taste to the juice. The cause of this limey taste has been frequently attributed to oxidation. If such is the case it would seem that the condition should be prevented by the presence of reducing agents. Experiments conducted at the University of California by Cruess and his students indicate that oxidation is not the cause of the limey taste. Immature oranges will yield bitter juice while oranges fully mature do not do so. The presence of a reducing agent, such as sulphur dioxide, when added as soon as the juice is pressed from the fruit does not prevent the formation of the limey taste, nor does a similar addition of carbon dioxide prevent its development. The addition of sugar to orange or lemon juice helps to retain the flavor, but does not result in a thoroughly saisfactory product. Juices which contain oil from the rind tend to develop a "turpentine" taste.

Lemon and grapefruit juices tend to darken in the bottle, especially if the bottles are not well filled. Darkening, in opposition to the development of the limey or musty taste, is apparently caused by oxidation and may be prevented by the addition of a small amount of sulphurous acid.

[1]United States patents involving preservation of fruit juices are: Hans Zurck, No. 1045245, November 26, 1912 (by heat); W. Rueff, No. 1066153, July 1, 1913 (with CO_2); E. Monti, No. 1758266, October 26, 1915 (by heat); C. E. Burke, No. 1097442, September 5, 1916 (with SO_2); A. Fonyó, No. 1207041, December 5, 1916 (with lactic acid); H. C. Gore, No. 1284187, November 5, 1918 (by absorbent black); P. R. Welch, No. 1258627, March 5, 1918 (by heat); F. L. Dunlap and R. Kuever, No. 1338684, May 4, 1920 (by proteolytic enzymes and heat); Max Henius and F. Mendelsohn, No. 1343915, June 22, 1920 (with SO_2).

The best and most palatable preserved juices seem to be those of the grapefruit and lime.

ORANGE JUICE

Yields and composition.—A number of tests of sound and of frozen oranges were made to determine the volume of juice which should be expected from a ton of fruit. The yields were obtained by crushing the pulp from weighed lots of oranges and pressing in a small meat press.

TABLE XV

YIELDS OF JUICE

Sample	Juice Percentage	Juice in Gals. per Ton
No. 715. Frozen Valencias	19.1	42.5
No. 717. Frozen navels	20.2	45.0
No. 1110. Sound Valencias	55.3	132.8

The unfrozen oranges yielded nearly as much juice as can be extracted from grapes; the frozen oranges only about 25 to 30 per cent as much. The loss of juice in the frozen fruit is not due simply to concentration by evaporation, but also to an actual disappearance of the juice with all its constituents as shown by analyses in Table XVI.

TABLE XVI

COMPOSITION OF JUICE

Sample	Total Solids (Per Cent)	Total Sugars (Per Cent)	Acid as Citric (Per Cent)
1. Juice of unfrozen fruit, 1912-13	13.9	11.3	1.42
2. Juice of frozen fruit, 1912-13	16.2	....	2.00
3. Juice of frozen fruit, 1912-13	13.8	11.0	1.40
4. Juice of frozen fruit, 1912-13	13.6	....	1.30
5. Juice of unfrozen fruit, 1912-13	13.0	....	.90
6. Juice of unfrozen fruit, 1912-13	12.0	....	.99

These data, showing that the concentration of the solids in the juice from the frozen and unfrozen oranges is about the same and the fact that there is a much greater quantity of juice in the unfrozen oranges, indicate a disappearance of both solids and liquid after freezing.

A comparison of samples 1 and 2 indicate a slight concentration due to evaporation, but samples 1 and 3 show practically the same composition. On the whole, the composition of the juice seems to be little affected by the freezing of the oranges.

Orange juice according to these analyses, shows nearly three times the amount of acidity found in grape juice and five or six times the amount

found in apple juice. The total solids are about two-thirds those of grape juice and a little less than those of apple juice.

Clearing.—The juice should be made permanently bright, so that it will have an attractive appearance when bottled. Fresh juice will not filter easily and is difficult to make bright by filtration until it has stood a certain length of time. The length of time necessary varies considerably, but, in all the tests made in the laboratory, twenty-four to seventy-two hours was the maximum variation.

The following observations bring out the effect of preliminary defecation by standing and settling on the clearing of the juice by filtration.

TABLE XVII

EFFECT OF STANDING FOR VARIOUS TIMES BEFORE FILTERING

Sample	Observations
1. Fresh juice	Filters slowly and filtrate is cloudy
2. Same juice after 18 hours	Filters slowly and filtrate is cloudy
3. Same juice after 52 hours	Filters slowly but filtrate is clear
4. Same juice after 76 hours	Filters easily and filtrate is clear

Other samples of juice behave similarly, except that in most cases the time necessary for defecation was less than the seventy-six hours noted in Table XVII. One sample became jelly-like in a few hours after expressing it from the oranges, but two days later the jelly-like material coagulated and settled out, carrying down all suspended matter, leaving a perfectly bright liquid above. Apparently a coagulating enzyme is active in bringing about the clearing of the juice. Further evidence for the existence of such an enzyme in orange juice is given by the fact that, if the juice is pasteurized, it will not clear, but will remain cloudy until filtered or clarified by other means. Many enzymes are destroyed by heat; therefore the fact that unpasteurized juice clears of its own accord and the pasteurized undefecated juice does not indicates the presence of such an enzyme.

Several samples of the same juice were treated as follows:

1. Defecated fifty hours and then heated in bottles to 185°F.

2. Defecated fifty hours, egg albumen added at the rate of 5 oz. per 100 gal., then heated in bottle to 185°F.

3. Defecated fifty hours, casein added at the rate of 5 oz. per 100 gal., then heated in bottle to 185°F.

4. Not defecated; casein added at rate of 5 oz. per 100 gal. immediately after pressing and then heated in bottle to 185°F.

5. Not defecated; heated in bottle to 185°F. immediately after extraction from the fruit.

Seven months later, samples 1, 2, and 3 were bright, but 4 and 5 were cloudy. These tests demonstrate the utility of defecation in clearing the juice. (Compare especially tests 3 and 4.) They also indicate that finings are unnecessary for the clearing of the juice. (Compare test 1 with tests 2 and 3.)

Three other small lots of juice were treated in the following ways:

6. Same juice as No. 5, defecated seventy-six hours with sulphurous acid, filtered, pasteurized at 185°F. in bottle. This juice came from unfrozen oranges.

(La Parfumerie Moderne)

(Petite Revue)

COLLECTING ORANGE BLOSSOMS IN FRANCE.

7. Juice from frozen oranges tested in same manner as No. 6.

8. Same juice as No. 7. Not treated with sulphurous acid. Filtered several times till bright and pasteurized twice at 185°F.

Seven months after pasteurization, samples 6, 7, and 8 were all bright. No. 6 was of a slightly lighter shade than No. 7. No. 8 was dark brown in color. Samples 6 and 7 exhibited very little cooked flavor; No. 8, on the other hand, had enough of the cooked taste to make it considerably inferior to samples 6 and 7. Although not treated with sulphurous acid, sample 8 did not have a very pronounced bitter flavor, probably because it was sterilized so soon after extraction, thus not allowing time for the development of the bitter flavor.

In the settling-out process, or defecation of the juice, two serious difficulties are met with. The first is that the juice will start to ferment if allowed to stand long enough to defecate, unless treated in some way to delay fermentation. Secondly, a bitter taste develops in the untreated juice if it is long exposed to the air. Tests have shown that the addition of moderate amounts of sulphurous acid will prevent fermentation for the desired length of time and will also prevent the development of the bitter taste. Since sulphurous acid acts in the opposite manner to the oxygen of the air, it may be surmised that the development of the bitter flavor in orange juice is due to the oxidation of some tasteless constituent flavor in juice to a bitter form. An experiment indicated that the sulphurous acid must be added very soon after the oranges are crushed in order to check the bitter flavor, as, in this particular test, a bitter taste was perceptible in one-half hour after the juice had been expressed. The amount of sulphurous acid necessary in any case will probably not exceed 2 or 3 oz. per 100 gal. of juice, or if reckoned in terms of the form in which it is most usually applied, not more than 4 to 6 oz. of potassium metabisulphite. The latter is most conveniently added as a water solution which is made up so that each gallon contains the amount of sulphite necessary for 200 gal. of the juice. For example, if it is desired to add 8 oz. to each 200 gal. a solution is made containing 8 oz. of the metabisulphite per gallon of water.

After the addition of the potassium metabisulphite, the juice may be allowed to stand in convenient containers until it has defecated long enough to permit rapid filtration. The amount of sulphites recommended are well below the limits allowed by law in various food products. It may also be stated that a great deal of the sulphurous acid disappears during subsequent treatment, so that the amount left in the juice is negligible.

Filtration.—After the juice has defecated a sufficient length of time, it may be filtered without difficulty to give a bright liquid. In this process, it will be necessary to draw off the clear liquid from the sediment. This juice can undoubtedly be filtered in a commercial way in any of the good filters that are on the market. A pulp filter is probably the best. The sediment from the defecating vessel may be thrown on bag filters and in this way brightened; it cannot be passed through the pulp filter (because of clogging) without a preliminary filtering through a bag filter.

Orange juice is much more easily filtered than grape or apple juice and gives on filtration a very brilliant liquid. This juice also differs from filtered fresh apple or grape must in that it remains bright after heating;

fresh grape and apple juices may be filtered bright but will often not remain bright after heating.

Pasteurization in barrels.—The juice must be pasteurized after filtration to prevent fermentation. It may either be bottled before pasteurization or may be pasteurized and stored in barrels until it is convenient to bottle.

If the juice is stored in barrels the latter must be new or must have been used only for juice and kept sterile by burning sulphur tapes in them when empty. Before filling, the barrels should be thoroughly steamed to sterilize the inner surface. Several forms of pasteurizers may be used in the heating of the juice to the desired temperature. One of the simplest types may be made by placing a non-corrosive metal coil in wooden container of convenient size. Juice may be placed in this container and steam passed through the coil. The coil should be kept in motion during the heating in order to avoid scorching the juice. A tin or aluminum coil will not be attacked by the orange juice. Double-jacketed aluminum kettles are used with success in the pasteurization of grape juice and apple cider, and would no doubt give satisfaction in the sterilization of orange juice. Steam is passed between the walls of the kettle to heat the juice.

Both of the foregoing heaters are discontinuous in their action. Where a continuous flow of sterilized juice is desired, a continuous pasteurizer may be constructed by placing a tin pipe inside of an iron pipe. Steam may be passed through the outer pipe and juice through the inner tin pipe. By varying the steam pressure and the flow of juice, the desired temperature may be attained. Continuous pasteurizers suitable for this purpose are obtainable.

In any case, the juice should reach a temperature of 185°F. It should then be run into clean barrels. The barrels should be bunged immediately with a new bung covered with a clean cloth. The barrel should then be rolled on its side to sterilize the bung with the hot juice. The flavor of orange juice seems less easily injured by overheating than that of grape or apple juice.

During the first few weeks of storage, the barrels must be carefully watched in order that those which start to ferment may be detected in time to save them. With careful work few, if any, should ferment.

Pasteurization in bottles.—Whether the juice is bottled immediately after filtering or stored first, for a time, in barrels, it must receive a final pasteurization after bottling. The bottles and corks and caps that are used must be clean. Capping is preferable to corking, because it gives less trouble in handling and gives a neater appearance to the bottle. There are two types of caps, the Crown cap or the ordinary beer bottle or soda bottle cap, and the Goldy stopper, the aluminum cap seen on grape juice and pineapple juice bottles. Of these the latter type is preferable. The bottles must be sterilized immediately after filling and capping. A convenient form of pasteurizer may be used by placing a false bottom in a rectangular wooden tank. Under the false bottom is placed a steam coil. The bottles are placed on the false bottom, water is admitted so that its level is about three-fourths the height of the bottles. The pasteurizer must be covered in order that the caps and tops of the bottles will be heated by the escaping steam. One bottle may be left uncapped. A thermometer is

placed in this bottle and the rise in temperature noted. The liquid in the bottles must reach a temperature of 180°F.

The bottles may then be removed and allowed to cool. They should be stored until it can be seen whether the pasteurization has been successful and whether any of the bottles develop cloudiness; three weeks or a month will probably be sufficient in most cases. In laboratory tests the juice pasteurized in bottles developed a slight sediment after three months, but so small in volume as to be scarcely noticeable.

To some, the unclarified juice might be preferable to the clear. If such a juice is to be produced, no filtration is necessary and the juice can be placed in bottles immediately, and sterilized. Its appearance would probably not be pleasing, hence would probably be disguised in dark bottles.

Summary.—It is recommended that the freshly expressed juice be allowed to defecate until it becomes fairly clear. To prevent fermentation during this period and to check the development of a bitter flavor, a moderate amount of sulphurous acid should be added to the juice immediately after crushing. Potassium metabisulphite is a convenient form in which to add the sulphurous acid. The defecated juice should be filtered. It may then be bottled immediately and pasteurized, or may be pasteurized in barrels and kept until it is desired to bottle it. The bottled juice should be sterilized at 180°–185°F. to prevent fermentation and mold growth, especially the latter.

GRAPEFRUIT JUICE

According to the Chace method, the fruit is washed, cut in halves or smaller pieces, and the juice extracted by means of a hydraulic press. It is then passed through about 100 in. of sterling silver tubing surrounded by boiling water, the time of passage being approximately five seconds. It goes immediately from this pasteurizer into a hot 5-gal. carboy which is filled as far as possible into the neck, leaving, however, a slight air space just beneath the cork. This is put in cool storage, the temperature not to exceed 50°F., and there kept until the sedimentation has finished, leaving a clear liquid in the larger part of the carboy. The clear liquid is decanted and treated with about 1 lb. of Kieselguhr per 100 gal., the Kieselguhr having been previously washed several times with boiling water until the extract is tasteless. The residues, after drawing off the supernatant liquid, are treated with about 5 lb. of Kieselguhr per 100 gal. of material, and filtered. Chace uses the ordinary rack-and-plate-filter press for this filtration, although he is not sure but other forms would probably be more rapid and give just as clear a product.

After this has been done, the juice is sweetened until the solid contents are about from 17 per cent to 20 per cent. This usually requires about 5 per cent of sugar, with grapefruit. The product is then again passed through the flash pasteurizer, using the same method as before. If the bottling is done hot care should be taken lest the paraffin melt off the Crown caps and deposit in the beverage. The grapefruit juice thus prepared remains clear for months. Recently a Jensen milk pasteurizer was substituted in the first process. This is considerably more rapid and permits of rapidly filling the carboys with the juice.

MIXED JUICES

Chace bottled several combinations of grapefruit with other fruit juices, and considered two of these blends as very good. Both pomegranate and loganberry juices make fine blends. He uses about 20 per cent of the blending juice to 80 per cent of grapefruit juice, and sometimes sweetens until the solids are raised to 20 per cent. This gives a product of brilliant color and fine flavor. He used infusorial earth as a filtering medium and a flash sterilization above 85°C. Juices have kept for six months without deposition of sediment or deterioration of flavor.

Other blends, with California grape juice, have been tried out by Chace but lack characteristic flavor. The muscats probably do better than the others, but all blends were inferior to the first two mentioned. Concord grape juice has not been tried, but there seems no reason why it would not blend well with grapefruit juice.

CONDENSED FRUIT JUICE[1]

Concentrated juices, if they could be satisfactorily produced, would have obvious advantages over unconcentrated juice. In the production of concentrated juices two dehydrating methods are usually employed, namely, by vacuum distillation or freezing. Neither of these result in a product which when diluted to its original volume with water has a satisfactory taste. The chief defect, apart from the loss of flavor, is in a darkening of the juice presumably from a carbonization of the sugar by the concentrated acid. The latter may be overcome by neutralizing the acid.

One firm in concentrating juice by vacuum distillation maintains a vacuum of 28 inches and a temperature of 108°–110°F. The final product contains 61–65 per cent citric acid.

The methods of concentrating the various juices will be discussed under the various localities involved, e.g., Sicily, West Indies, and Florida. Dehydration by freezing has not been used widely. As it seems to have advantages over any other process used so far, a detailed description will be given here with the hope that its use will be stimulated.

[1]United States patents involving the concentration of fruit juices by means of cold are: A. Gürber, No. 723152, March 17, 1903; E. J. Sheehan and W. S. McKay, No. 1211361, January 2, 1917 (addition of sugar); M. O. Johnson, No. 1362868, December 21, 1920 (addition of sugar). United States patents involving the concentration of fruit juices by means of heat are: C. Graef, No. 640289, January 2, 1900; R. Oehme, No. 950950, March 1, 1910 (with solvents); A. Fernbach, No. 981405, January 10, 1911 (in CO_2); P. Kestner, No. 1005554, October 10, 1911; J. N. G. Singleton, No. 1093081, April 14, 1914; H. C. Gore, No. 1141458, June 1, 1915; J. L. Kellogg, No. 1189127, June 27, 1916; A. C. Braden, No. 1278297, September 10, 1918 (addition of sugar); C. A. Kern, No. 14633, April 15, 1919. United States patents involving the concentration of fruit juices by desiccation are: L. C. Merrell, I. S. Merrell, and W. B. Gere, No. 878977, February 19, 1908; W. S. Osburn, No. 1088267, June 4, 1912; C. Ellis, No. 1068047, July 22, 1913; C. E. Gray, No. 1057935, October 26, 1915.

Concentration of fruit juice by dehydration by means of cold: the Gürber method.—Perhaps the first patent for concentrating solutions in this manner was applied for by August Gürber in Germany, July 15, 1899. Later (1903) he received a United States patent for the process. A liquid to be concentrated is placed in a suitable centrifugal machine, preferably having a central coil or chamber containing a refrigerating medium, such as ammonia, brine, or the like. The centrifugal machine is then started, and as the freezing action proceeds, the watery constituent of the liquid is congealed into ice crystals, which crystals are, by reason of their less specific gravity, displaced by the heavier solids and caused to accumulate about, and adhere to, the central coil or refrigerating chamber, the more concentrated solution, deprived of a large portion of its water, finding its way to the outer periphery of the drum, whence it may be drawn off in any well-known manner. The product may be withdrawn at an intermediate stage of concentration and subjected to further similar treatment or the exit valves may be so adjusted as to accomplish the desired high degree of concentration in one and the same continuous treatment by subjecting the contents of the drum to the action of refrigeration and centrifugal separation during a sufficiently extended space of time.

Concentration of fruit juice by dehydration by means of cold: the Monti process.—If we consider that the evaporation of one kilo of water at 15°C. requires theoretically 600 positive calories, while the separation of one kilo of ice from a solution cooled to 0°C. requires only 40 negative calories, it is plain in view of the progress in methods of refrigeration that there would be a theoretical gain on an industrial scale in substituting for direct evaporation by heat the freezing and separation of the water in the state of ice as a means of concentrating large volumes of dilute solutions.

In this field, Italy has contributed, largely through the numerous investigations of Endo Monti, to the progress of the concentration of liquids by means of cold.

During the winter of 1902, Monti was seeking a practical and economical method to concentrate the weak wines of 1901. He found that on freezing the wine, and then inverting the vessel, keeping the bottom part insulated, and allowing the ice to melt slowly in the upper part, he obtained at first a concentrated wine, then wine progressively more and more dilute until finally a cake of ice crystals was left containing no soluble matters, but only tartar, lees, and other insoluble matters.

Monti noticed also that the first liquid to drip from the ice was much more concentrated than the liquid which remained uncongealed in the center of the vessel. In later experiments on a larger scale made at the establishment of the Italian Society for Artificial Ice, he demonstrated that, by passing the dilute liquids obtained in a previous operation and cooled to 0°C. through the mass of ice crystals, he could free the ice of all soluble matters without melting the crystals. Studying, later, this fact established experimentally, he demonstrated by a very simple experiment that when a solution is frozen rapidly, the dissolved substances are concentrated not in the uncongealed portion of the liquid, as formerly supposed, but in the water interposed between the ice crystals, and only later and slowly do they diffuse into the uncongealed liquid. He took three metallic cylinders

about 10 cm. in diameter and 20 cm. in height closed at the bottom. These he filled with equimolecular solutions (one-tenth moleculegram to 100 gm. of water) of alcohol, saccharose, and citric acid and immersed them in a freezing mixture of about 18°C.

At the end of an hour a little more than half of the liquid was frozen, forming a ring adhering to the walls of the vessel. On removing 50 c.c. of the liquid and determining its density with a Mohr's balance he found that there had been no sensible change and therefore no concentration. After pouring out the uncongealed liquid, he placed the frozen contents of each cylinder on a funnel and drained off liquids which showed a concentration double that of the original solution. In another experiment, instead of pouring out the uncongealed liquid and draining the ice on a funnel, he surrounded the vessel with cotton and left it for several hours and found that the density of the uncongealed liquid gradually increased and its temperature fell as the cold, concentrated solution between the ice crystals gradually diffused into the liquid in the center.

In other experiments he froze various solutions (wine, beer, coffee, meat extract, etc.) in insulated cylinders of convenient height, furnished with an opening at the bottom. By allowing the dilute, cooled solutions obtained by allowing the ice in the upper part of one cylinder to melt and to filter through the ice of another cylinder containing the same solution he was able to displace completely the concentrated solution between the crystals without melting more than a very small part of these crystals. At each operation he obtained pure ice at the top of the cylinder while extracting a concentrated solution from the bottom. The solutions of an ever increasing degree of dilution which served for the extraction were reproduced without increase of volume for an indefinite number of successive operations.

Monti showed further that if the cooling was pushed too far the permeability of the mass diminished, the dissolved substances precipitated or crystallized in the interpolated water and the extraction become more and more difficult and finally impossible. The limits of cooling varied with the concentration and with the viscosity of the solutions, and were in the case of fermented liquids about three times the temperature expressed in negative degrees centigrade, at which the solution commenced to freeze. With grape juice and concentrated solutions the limit was about twice the freezing temperature and in all cases the point of congelation of the saturated solution.

For this reason, it is advisable to limit the congelation to the separation of 60 to 65 per cent of the ice in dilute solutions and 40 to 50 per cent in more concentrated solutions. When a greater concentration is desired, it is best to obtain it by two or more successive operations. In the particular case of sugar solutions he found that when the syrup contains over 50 per cent of sugar, the extraction becomes very slow and difficult, owing to the viscosity of the liquid.

Practically eighty-eight negative calories are needed for every kilo of ice to extract 60 per cent of the ice from each 10 per cent sugar solution at 2°C. by freezing at 3°C. A 25 per cent solution frozen at −6°C. requires ninety-five negative calories to extract 45 per cent of the ice.

To this amount of calories must be added about 10 per cent to allow for the heat of the vessels and tubes and for the ice which melts, owing to the imperfect insulation of the apparatus and the imperfect exchange of temperature in the coils.

Monti obtained various patents for the application of his method to the concentration of diverse liquids and grape must.

By a method patented April 17, 1906, he prepared concentrated must from freshly crushed grapes from which the juice was extracted and cooled rapidly before the flavor changed. He prepared four aromatic musts from various varieties of grapes, Dolcetto, Banarda, Freisa, Nebbiolo, Moscatello, and preserved them at ordinary temperatures after pasteurizing at 50°C. in bottles sealed with paraffin. These concentrated musts which are fluid and perfectly clear taste very delicate, recalling in the highest degree the true, natural aroma of the grape.

The characteristic of the Monti patents which distinguishes them from others dealing with concentration by the application of artificial cold, is the extraction of the soluble substances interposed between the ice crystals by means of osmosis and progressive extraction with solutions of increasing degree of dilution obtained by the fractional liquefaction of a previous operation. Naturally these solutions must be cooled to the point of freezing with the ice separated in the preceding operation. This is accomplished automatically without mechanical work and therefore economically. By a patent of 1908 Monti has still further simplified the construction of his apparatus by suppressing coils and cocks, so that the whole can be made by ordinary country blacksmiths and mechanics and adapted to any form of freezing machine.

With regard to cost, Monti has demonstrated that his process is more economical than those of evaporation by heat or in vacuum. This supposes that the motive power does not cost more than $40 per horse-power per year and that efficient freezing machines are used which with a suitable supply of refrigerating water are capable of absorbing at least about 2,000 calories per horse-power per hour. In this regard Monti makes the following statements:

"It was shown that with a concentration plant of moderate size, not more than 120 frigories were used for every kilo of water extracted, representing 36 kilos of fuel for each hectoliter while the direct evaporation of one kilo of water required 720 calories representing 1.25 kilos of steam and 150 kilos of fuel for each hectoliter. This indicates that evaporation requires about four and one-half times as much fuel as congelation for the separation of the same amount of water. In each case, proper allowance is made for all losses based on the average results of a continuous operation on an industrial scale.

"Moreover, the cost of present installation of apparatus for concentration and the buildings necessary for refrigeration, conservation, and clarification of the musts and wines is much exaggerated, as it is based on imperfect construction and unfavorable working conditions.

"In fact, the installation of an ice plant of the capacity of 25 hectoliters per day of four extraction columns made of reinforced concrete and properly insulated of 250 hectoliters each, of which three are used to concen-

trate 250 hectoliters of must or wine per day and the fourth as a reservoir for the frozen water, and the recuperators necessary for the refrigeration of the wines and the extraction liquids with the cold water of the separated ice costs less than $2,000. The tinning and varnishing of the 1,000 ice forms needed cost less than $600. Assuming, therefore, that the factory works 180 days producing ice and concentrating the must or wine, 27,000 hectoliters would be handled in six months which reduces the cost of the plant to 20 cents for each hectoliter of must or wine concentrated. This cost corresponds to 2 cents per hectoliter if we calculate on amortization in ten years.

"The labor cost is also much reduced by the suppression of centrifugal extraction and the movement and filling of forms. The extraction of the ice is accomplished automatically by the crane used in all ice factories of any size.

"It is true that the tinning and varnishing of the forms must be renewed at rather frequent intervals and a part of the amortization and interest on the cost of the plant must be charged against the concentration.

"Where an ice factory is not available the cost of the plant is naturally greater. However, wooden concentrators with straight aluminum or tinned copper tubes are of such simple construction that they can be made anywhere by skilful mechanics. The cost of a concentrator of the capacity of 50 hectoliters should not exceed $800 in any case. A battery of four, of which one would serve as a reservoir for the frozen water, would cost $3,200. Reckoning $2,400 as the cost of a freezing machine capable of absorbing 20,000 calories per hour, it follows that the cost of a plant to concentrate 50 hectoliters a day or 15,000 hectos per annum, varies, excluding the cost of the buildings, from $6,000 to $8,000 or 50 cents per hectoliter, according to local conditions. This with a ten-year amortization represents an expense of 5 cents per hectoliter of wine concentrated. The cost of cooling and conserving wines and musts in cold storage is much higher.

"In buildings of a capacity of from 20,000 to 40,000 hectoliters, such as might be established in Italy for the treatment and storage of wines and musts in refrigerated containers of reinforced concrete, an area of 1 sq. m. for each 10 hectoliters may be reckoned, representing an expense of 20 cents for each hectoliter of must treated. Provision also must be made for the refrigeration of the rooms and containers.

"This refrigeration, assuming a maximum difference of 30°C. between the inside and outside temperatures, would necessitate the absorption of 15 calories per hour per cubic meter, that is, 1.5 calories per hectoliter or per 30,000 hectoliters, 45,000 frigories per hour.

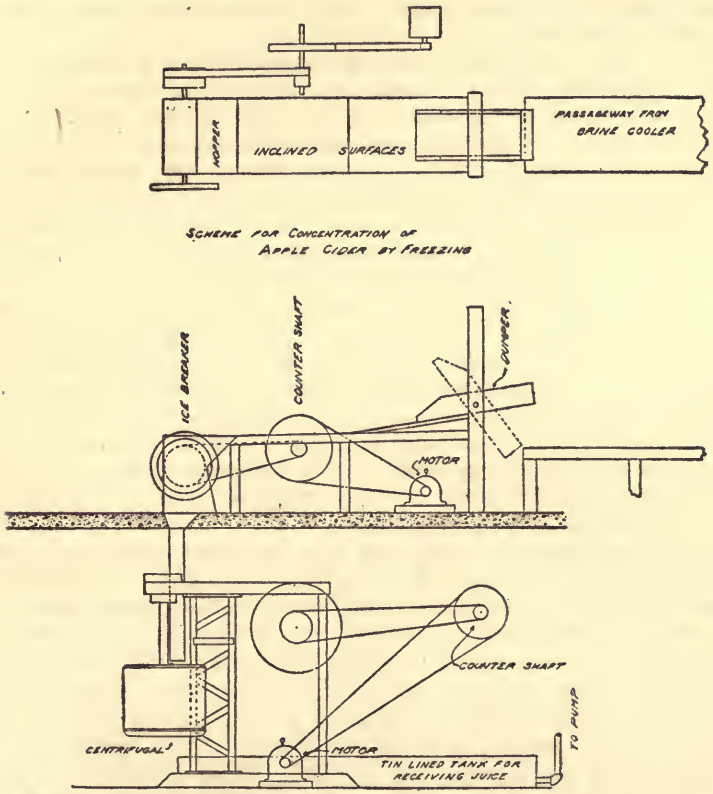
"It will be necessary, therefore, in this case to provide for the absorption of 100,000 calories per hour which would require a force of about 50 horse-power.

"It should be noted, however, that the unit cost of plant and running expenses of the establishment and freezing machinery increases rapidly as the output of the plant diminishes. And also, with equal productive capacity the unit cost may be doubled or quadrupled, if the warehouses and reservoirs are not planned to completely utilize the space, or if the ice machines and the insulation of the walls is not as perfect as possible. Under normal

conditions, therefore, the conservation in cold storage costs twice as much as their concentration.

Concentration of fruit juice by dehydration by means of cold: the Gore process.—This process of concentration of cider by freezing has become quite popular. For this reason it is given here as a possible means of concentrating citrus fruit juice.

An ice-making plant was equipped with special 300-pound tin-lined freezing cans, an ice crusher, a centrifugal machine, necessary machinery for handling the frozen cider, and containers for the finished product (Fig. 13).



(Gore: Yearbook, U. S. Dept. of Agric.)

FIG. 13.—Dumper, ice-breaker, and centrifugal machine used in crushing and centrifugalizing frozen apple juice.

The fresh cider is placed in the tin-lined ice cans and frozen in the brine tanks of the ice-making plant. For the first freezing the brine temperature should range between 10° and 20°F., which will freeze the cider into a solid mass in from thirty-six to forty-eight hours. The frozen cider is then loosened from the cans by removing it from the brine tanks, thawing it at the sides and bottom, and dumping it, just as ice is removed from the

cans in ice-making. The blocks of frozen cider are then passed through a power ice crusher which breaks them into pieces no larger than a walnut.

The crushed frozen cider drops from the crusher into a standard sugar centrifugal machine which provides a mechanism for rapidly whirling it, and thus separating the syrupy part from the water ice, just as in the case of sugar, where the molasses is whirled off from the crystallized sugar. The frozen cider drops into the perforated metal basket of the machine. This basket, which is whirled rapidly, causes the syrupy part of the cider to fly off from the mass of ice into the collecting chamber opening into the collecting tank below. A centrifugal operating at about the same speed used on sugar will separate most of the syrupy content from a charge of ice in three minutes.

The partially concentrated cider in the receiving tank is then put again into the freezing cans and refrozen at a temperature from 0° to 10° F., which will refreeze the syrupy cider in from two to three days. The refrozen cider does not become very solid and can readily be removed from the cans without thawing. It is passed through the crusher and again whirled in the centrifugal machine and reaches the receiving chamber as a fairly thick, somewhat viscous syrup. One gal. of this syrup represents 5 gal. of the original cider, which means that nearly 4 gal. of water have been removed by freezing and centrifugalizing.

As the ice remaining in the centrifugal basket still contains some of the sugar and solids of the cider, it may be removed from the basket by use of the unloader provided, allowed to warm up slightly, and again be run through the centrifugal machine. This will remove practically all the valuable material. As there will now be less than 1 per cent of apple solids left in the ice, it probably does not merit further treatment. The concentrate obtained on the second centrifugalizing of the ice is somewhat richer in solids than ordinary cider and may be added to the fresh cider or refrozen and treated as fresh cider.

The fully concentrated cider will be a somewhat thick liquid with the cloudy appearance and color of unfiltered fresh cider. If kept sealed at household refrigerator or in cold-room temperatures, it will gradually ferment, but will spoil much more slowly than ordinary cider. Concentrated cider intended for use during the following spring or summer should be put into cold storage at once and kept at or below 32°F. It can be shipped anywhere in winter weather in unheated cars without danger of spoiling. It can be bottled, canned, or shipped in clean kegs. Inasmuch as a 1-gal. can represents 5 gal. of cider, the equivalent of 250 gal. of fresh cider can be shipped profitably for much longer distances to market than can the bulky fresh cider. In addition to saving 80 per cent on the freight, the reduction in volume permits the shipper to use containers one-fifth the size, which is an important saving in cooperage. The saving in containers, which have always been relatively expensive items in shipping cider, should alone nearly offset the cost of freezing and concentration. In addition there is the saving of drayage and other handling costs. On its arrival at the market the retailer can at once restore it to cider by adding four parts of water, or he can sell it in the convenient concen-

trated form to his customers. Moreover, as has been explained, this cider, instead of fermenting on the journey, or a day or two after its arrival, will keep for two or three weeks in closed containers if not allowed to get warm, and if kept closed in an ice box or refrigerator will remain in good condition for five or six weeks. The cider in its concentrated form is useful also as a flavoring syrup for desserts. When stored at low temperatures, the concentrated cider will keep indefinitely. In this way concentrated cider made in the fall can be kept over and used in the soft-drink trade during the hot months, at soda fountains, and in the home.

Those who wish to make a clear, brilliant cider concentrate can filter it by adding to the concentrated product 3 per cent or more by weight of infusorial earth, which should be thoroughly stirred in. This mixture can then be pumped through a plate-and-frame filter press, such as has been described in connection with the manufacture of apple syrup.

a) *Cost of concentrating by freezing.*—Until the process is well worked out on the commercial scale, statements of the probable cost of preparation are necessarily estimates only. The principal elements of cost are cost of raw material, cost of freezing, labor, power, interest, depreciation, and superintendence.

b) *Cost of raw material.*—Apples should yield at least 150 gal. of cider per ton, with apples at $6 per ton, allowing 2 cents per gallon as the cost of pressing, the raw material charge is 6 cents per gallon, or 30 cents per gallon of finished cider concentrated by freezing, on the assumption that the reduction in volume is 5 to 1.

c) *Cost of freezing.*—If the brine tanks of a modern ice plant can be used, the cost of freezing for the first time, including dumping and delivery to the ice crusher, should not exceed $3 per ton of cider measuring about 230 gal., provided ice-making is carried on during the balance of the year, so that the yearly fixed charges of the ice factory are borne by cider and ice in proportion to the amounts frozen. In the second operation about one-third of the original volume of cider is refrozen, bringing the total cost of freezing up to $4 per ton, approximately, or 8.7 per gallon of concentrated cider. Where an ice plant is to be erected for the purpose of freezing cider alone, using it at full capacity for but a few months each year, the cost of freezing will necessarily be much higher.

d) *Labor cost.*—Two men, with the assistance of the engineer at the ice plant, whose labor is included in the cost of freezing, can easily operate the centrifugal machine at the rate of 300 lb. of frozen cider per ten minutes, amounting to a little more than 7 tons per eight-hour day. About one-third by volume of the original cider is returned for refreezing. On the following day the ice obtained on the day previous is recentrifugalized, requiring about a half-day's work, and two days later the centrifugalizing in the second operation, requiring about a half-day's work, is accomplished, producing cider concentrated by freezing in finished form, except for filtering, which may or may not be done, at the option of the manufacturer. Thus, approximately two days' work of two men is required in working up 7 tons, about 1,600 gal., of fresh cider, or 320 gal. of cider concentrated by freezing. At $2.50 per day the labor charge is thus $10, or 3.12 cents per gallon. The power required for crusher and centrifugal machine and for

small hoist for elevating the ice for recentrifugalizing totals less than 100 horse-power. The crusher requires 2 horse-power, centrifugal 5 horse-power, and hoist 2 horse-power. The centrifugal costs $560 complete and the ice crusher $84. These are the prices paid by the department on competitive bids for a 30-in. centrifugal and a standard crusher for 300-lb. blocks of ice. Erection of the equipment and necessary pumps and vats for economically carrying out the process should bring the equipment cost to between $1,000 and $1,500, not including the cost of the building. A plate-and-frame filter press and feed pump costs about $300. It is worth while to call attention to the fact that centrifugal and ice crusher, as well as hoist, filter press, and feed pump are made to stand heavy, constant service.

We thus have the following estimate of cost per gallon for the preparation of cider concentrated by freezing:

	Cents
Raw material	30
Freezing	8.7
Labor	3.12
	41.82
Filtering, power, interest, depreciation, and other charges	8.18
Total	50.00

The cost items classed under filtering, power, interest, etc., cannot be determined at the present time with anything like accuracy. They will necessarily vary with the volume of cider concentrated. On the whole, however, a cost figure of 50 cents per gallon is a conservative estimate for the preparation of cider concentrated by freezing, on the assumption that the brine tank of a going ice plant is available for the freezing.

Concentration of fruit juice by dehydration by means of heat: the McClendon-Dick process.—A unit or dehydrating cell of J. P. McClendon and E. M. Dick consists of an octagonal chamber 20 ft. in diameter and 20 ft. high with twelve hot-air ports in three tiers. The upper tier admits air at a velocity of 300 ft. per minte, the middle at 600 ft., and the lower 150 ft. The centrifugal spray is in the center and just below the level of the upper tier of ports. It consists of a hollow shaft (admitting the juice) and a head made of a series of concave disks serrated at their margins (12 in. in diameter). Between the disks is a series of grooved collars distributing the juice from the hollow shaft to the concave sides of the disks. The shaft and head rotate on ball bearings 5,000 revolutions per minute and transform the juice into a fine spray or fog. The air currents cause eddies and retard the falling of the spray until it is dried. The exhaust ports are at the bottom of the cell and are so large as not to retard the falling of the dried juice in the dead air space. The incoming air is heated to 55°–70°, but the evaporation on the surface of the droplets prevents their reaching this temperature before they fall into the dead air space where the temperature is lower. Since the droplet is exposed but one minute to the hot air, any temperature effect on the vitamine is mini-

mized. Orange juice is one-eighth solids. If it is evaporated to one-fifth of the original weight the pectin forms a clot from which a syrup oozes. This separation is not hastened by the centrifuge but is by a filter press. If the juice is evaporated to one-sixth or less, no clot separates. The high content in monosaccharides makes it hygroscopic when dried. The taste is practically unaffected and the dried juice, reconstituted with water, makes a pleasant drink. Cane sugar may be added before drying.

Milk is dried in the same type of cell and the orange preparation may be added to milk powder to restore the antiscorbutic lost in pasteurization. (The milk is first pasteurized since wild yeasts and some bacteria are not killed by drying.) The orange juice imparts a lactic acid flavor to the reconstituted milk in proportion to the amount added, but the milk does not curdle unless enough citric acid (juice) is added to bring it to the isoelectric point of casein.

FERMENTATION PRODUCTS

The citrus fermentation products[1] so far known commercially and experimentally are based primarily upon alcoholic and citric fermentations. Only citrus fruits of appreciable sugar content, can therefore, be used, and fermentation products are usually derived from oranges, though yielded also by grapefruit. The products in question are four: alcohol, wine, vinegar, and acetone. Alcohol as such is seldom made from citrus fruits. The preparation of "wine" is the first step in the manufacture of vinegar and of acetone from citrus fruits.

FERMENTED JUICE FOR VINEGAR-MAKING

Orange wine may be defined shortly as the product of the alcoholic fermentation of oranges and the usual wine cellar treatment.

The samples of orange juice examined at the Zymological Laboratory of the University of California have averaged by chemical test about 11 per cent actual total sugars. On fermentation this would give about 5.5 per cent alcohol if the fermentation were carefully conducted.

Control of the micro-organisms.—Given oranges of suitable composition, the quality of the wine depends on the work of micro-organisms. The art of the wine-maker consists almost entirely in the control of these micro-organisms. His success in facilitating the work of the useful form (true wine yeast) and in preventing or hindering the work of injurious forms determines the quality of his product.

a) Before fermentation.—On the skins of sound ripe oranges as they hang in the orchard the micro-organisms are comparatively few

[1]This chapter in so far as it touches upon matters not directly applicable to the preparation of wine for subsequent vinegar or acetone making is to be regarded in the United States and in some of its territories as of purely theoretical and historical interest.

The production of citric acid by fermentation of sugar is discussed on p. 151.

TABLE XVIII

VARIATION IN COMPOSITION OF ORANGE JUICE

Sample	Total Solids (Balling Degrees)	Total Acid	Sugar (Per Cent)
Frozen Valencias, Riverside, 1912-13.....	12.2	1.5	....
Frozen Valencias, Riverside, 1912-13.....	13.8	1.4	11.0
Frozen navels, Riverside, 1912-13.....	16.1	2.2	....
Unfrozen navels, Los Angeles, 1912-13....	13.0	.9	....
Unfrozen navels, Los Angeles, 1912-13....	13.9	1.42	11.3
Unfrozen Valencias, Tulare, 1913-14.....	13.5	1.5	....
Unfrozen navels, Tulare, 1913-14.....	11.5	1.3	....
Unfrozen navels, Redlands, 1913-14.....	12.1	.9	....

and in an inactive condition. When ordinary care is exercised there is little danger that they will injure the wine. On broken or injured oranges the number is greater and the forms more active. If many such oranges occur they should not be mixed with the sound fruit if the best wine is to be made, even though it be designed for subsequent vinegar making.

Care should be taken to avoid unnecessary bruising of fruit which cannot be worked immediately. Cleanliness is essential throughout the process. Oranges, gathered in moldy boxes, hauled in dirty wagons or cars, and passed through dirty crushers, conveyors, and presses, may be so completely infected with injurious germs that it is impossible to obtain a good fermentation. Dust or soil is less injurious and, if excessive, may often be removed by sprinkling. Washing with antiseptics is not permissible. A weak solution of potassium metabisulphite might be used with benefit if it were not for the difficulty of regulating the amount of sulphurous acid entering the fermentation vat.

If the oranges have to be kept for some time before crushing they should be kept as cool as possible to delay the growth of molds. Gathering in the cool of the morning is desirable, and if oranges are gathered when warm they should be left in boxes to cool off during the night whenever possible. If the fruit is cool when it reaches the fermenting vat its temperature will neutralize a certain proportion of the heat of fermentation, and accordingly the difficulties connected with an injuriously high temperature are diminished.

However carefully the oranges are handled, a certain amount of dust, containing germs and other injurious matter, will reach the vats and presses. It is desirable to get rid of this matter before fermentation. This is best accomplished by settling and decantation.

When whole, unpeeled fruit is used, the presence of the oil from the peel greatly depresses fermentation. This oil can be eliminated by boiling before inoculating, however, at the risk of impairing the natural flavor.

Thorough crushing is necessary as the must should be well saturated with air. As the juice runs from the press it is pumped into a settling tank or cask. If it is cold, below 15°C. and of full normal acidity, the impurities may settle in twenty to forty-eight hours. If the temperature is higher than 15°C. and the acidity low, molds and yeasts will develop or fermentation will start and interfere with the settling. To prevent such interference a slight sulphuring with the fumes of burning sulphur or with a solution of potassium metabisulphite is usually necessary at this stage. The sulphuring should be as light as possible with acid musts, as it tends to preserve the fixed acids. For the same reason it benefits musts of low acidity. In from twelve to twenty-four hours the must should become purged of all its gross impurities including micro-organisms, and solid particles derived from the skins, stems and pulp of the oranges.

This separation of undesirable substances, the so-called "defecation," is of great value, ridding the must of extraneous matter that would affect the flavor of the wine in the heat of fermentation and eliminating the excess of protein that would serve as food for injurious bacteria. Centrifugal machines have been devised to hasten the process, but their work is not perfect.

Sterilization by heat has been tried for the same purpose but with indifferent success. A high temperature causes caramelizing of a part of the sugar and oxidizes the must, thus injuring the flavor. Discontinuous heating at lower temperatures in an atmosphere of carbon dioxide is efficient, but troublesome and expensive; all methods involving heat have the defect of extracting undesirable substances from the solid matters which are heated with the must.

Chemical sterilization is still less practicable. No substance could be used for this purpose except sulphur dioxide, but this can be employed only in minute quantities without seriously injuring the flavor of the wine.

All the methods discussed have for their object the diminution or elimination of micro-organisms of all kinds, and to the extent of their removal the true yeast is also lost. Hence the more efficient the method used, the more necessary it is to add wine yeast. Without this addition, in fact, all the precautions described may result in harm, for the wine yeast, being present in much smaller quantity than many of the injuri-

ous forms, may be completely eliminated, while enough of other forms of micro-organisms are left to spoil the wine after this is drawn off into clean casks for fermentation.

In order that the proper kind of fermentation may be initiated a "starter" of some kind is, therefore, added to the defecated must. An improvement on a natural starter is a pure culture of tested yeast. The methods of handling this would require too much space to describe here, but they are simple and such as could easily be devised by anyone with some knowledge of microbiological technique. They do not aim at obtaining an absolutely pure fermentation, which is unnecessary, but endeavor to have an overwhelming proportion of a thoroughly tested and suitable yeast which will attenuate the wine rapidly and perfectly before the injurious micro-organisms present have time to do any harm. This starter is used only for the first vat or cask. Those following are started from the first fermentations, care being taken always to use the must from a tank only at the proper stage of fermentation and to avoid all tanks that show any defect.

If grown in well-defecated and sulphited juice, the yeast will remain sufficiently pure, throughout the season[1]

The following figures were obtained in laboratory fermentations of orange juice.

Sample No. 1 was fermented with pure yeast; No. 2 was allowed to ferment naturally. Although the Balling was 1.6 per cent higher in the latter case, the yield of alcohol was only .3 per cent higher, indicating a greater efficiency in the pure yeast fermentation. It may be stated that the natural fermentation of No. 2 was carried on largely by undesirable types of yeast. This also happened in most cases where the juice was

TABLE XIX

YIELDS OF ALCOHOL FROM ORANGE JUICE

Sample	Balling of Juice (Per Cent)	Possible Alcohol (Per Cent)	Alcohol Obtained (Per Cent)	Loss due to Natural Yeas (Per Cent)
1. Pure yeast fermentation.....	11.2	4.25	4.25	...
2. Natural fermentation.....	12.8	5.18	4.5	.68

allowed to ferment spontaneously. In Sample No. 2, a heavy growth of film-forming yeast developed, giving a disagreeable flavor as well as causing the liquid to clear very slowly after fermentation. On the other hand, the juice fermented with the pure yeast, had a clean flavor, and was easily cleared.

[1]Formerly, directions always accompanied the wine-yeast distributed by the Enology Laboratory of the University of California.

b) During fermentation.—However carefully the injurious germs have been excluded and the proper yeast increased, fermentation will not be successful unless conditions are maintained as favorable as possible to the wine yeast and unfavorable to other micro-organisms.

The temperature of the crushed oranges or of the expressed must is of importance. If it is below 15°, unless the weather is warm, the oranges should be warmed to 20° or 25°. If this is not done, the molds and the undesirable *Saccharomyces apiculatus,* which require less heat than the wine yeast, *S. ellipsoideus,* will develop more quickly. This is of especial importance when starters are not used. Once the impurities are removed by the preliminary defecation the must is ordinarily not too warm for the commencement of fermentation. However, the warmer the must, the more artificial cooling will be necessary later, and the sooner this will have to be applied.

At the beginning of fermentation the must should be thoroughly saturated with air to insure the multiplication of the yeast. The aeration received in the first process of crushing and pressing the fruit is usually sufficient for this purpose. One objection to the sterilization of must by heat is the expulsion of the air and the difficulty of replacing it in the proper amount. Too much aeration on the other hand is harmful by injuring the flavor and color of the wine through over-oxidation and by promoting the growth of injurious aerobic organisms.

The proper employment of sulphurous acid in the regulation of fermentation is one of the most important but least understood parts of the wine-maker's art. Only by its proper use can wholesome wine of the highest quality be produced, while improper use of sulphurous acid will injure or completely spoil the wine. Its beneficial effects are due not only to its action on micro-organisms, but also to its influence on enzymes and on the color of the wine.

In the small quantities properly used in wine-making, it is antiseptic in a degree varying with the amount. All micro-organisms are susceptible to its action in different degrees. Bacteria are particularly sensitive, molds and pseudo-yeasts less so, while wine yeast is the most resistant of the usual forms found in must and wine.

Its effect on the color of wines is also of importance. By the action of oxygen, the color of wine is gradually darkened; this is prevented or much diminished by the use of minute quantities of sulphurous acid.

The most commonly used source of sulphurous acid is fumes of burning sulphur. Sulphur is burned in a cask and the must caused to take up the fumes by being pumped into the cask through the upper bung hole.

The method is defective in many ways. It is impossible to tell within very wide limits how much sulphur dioxide has been absorbed by the wine. Moreover, the sulphur burns incompletely and the volatilized sulphur acted upon by the yeast may produce sulphuretted hydrogen. Other sulphur compounds are also produced during the burning to some of which the so-called sulphur taste of wine is said to be due. Several devices have been invented to decrease these defects but none removes them completely and progressive wine-makers are adopting more reliable sources of sulphur dioxide.

An improvement is the use of potassium metabisulphite ($K_2S_2O_5$), a salt which can be obtained in the requisite purity in commerce, and contains 50 per cent by weight of sulphur dioxide. The amount of potash added by this salt in the quantities required is very small, and well within the limits of variation of the normal potash content of different wines. By the use of this salt, exact amounts of sulphur dioxide can be applied. Other sulphites are not permissible.

The best source of the acid, however, is the liquefied gas recently brought into limited use and manufactured comparatively cheaply in great purity. By the employment of this all the action of sulphurous acid is obtained and all uncertainty eliminated.

Some oranges, owing to their composition, especially their high acidity, are very resistant to the attacks of injurious bacteria. Others, owing to low acidity or highly nitrogenous nature, are more susceptible.

The quality and character of the wine depends greatly on the temperature of fermentation. If too low, the fermentation may be unduly prolonged, the wine yeast may have difficulty in overcoming its competitors and the wine may remain inferior and cloudy. On the other hand, if the temperature is too high the results are worse. The growth of bacteria is promoted, injuring the wine by the production of volatile organic acids, by displeasing flavors produced and by preventing the proper action of the yeast. Such wines may remain sweet on account of the failure of the yeast to do its work and become unpleasantly acid owing to the volatile acids produced by the bacteria.

Some means of controlling the temperature is, therefore, always needed. Where heat is deficient it may be supplied by direct heating of the must or part of it, or by heating the cellar. Small fermenting vats promote radiation, diminishing the heat, and cooling machines may be applied directly to the fermenting wine.

The main part of the fermentation should be completed in from three to five days. If it is desirable to retain the slight sweetness due to a small amount of unfermented sugar, this may be accomplished by

the judicious use of sulphurous acid, prompt clarification by filtration or by "fining" and, when necessary, by pasteurization. The pasteurization tends to remove those proteins which are coagulated by heat and which are the preferred food of bacteria.

In the case of dry wines, protection from bacteria is best obtained by prompt and complete attenuation. Fermentation should not be allowed to cease until all the sugar has disappeared. For this purpose, one or two aerations by pumping over may be required immediately after the end of the tumultuous fermentation. The temperature of the wine should not be allowed to fall sufficiently to check the action of the yeast until all the sugar has disappeared.

c) *After fermentation.*—As soon as all the sugar has been destroyed, in the case of dry wines, or when the desired degree of attenuation has been obtained in the case of sweet wines, all the useful work of micro-organisms has been accomplished. The quality and safety of the wine then depend on freeing it from the organisms present and preventing the entrance and action of all others.

As soon as bubbles of carbon dioxide cease to be given off, the yeast and other solid matters will settle to the bottom and the liquid become clear. This often occurs before the fermentation is complete. In this case the yeast should be stimulated by aeration as described above.

If the wine is dry it should be racked (drawn off, decanted) from the sediment into clean casks. The first racking is usually done to remove the more bulky sediment while the wine is still slightly cloudy during the first month or six weeks. If left too long on the yeast the autophagy or degeneration of the latter may produce substances which injure the brightness and flavor.

A second racking is necessary at the end of the winter before the spring rise of temperature tends to renew the activity of the micro-organisms which always remain in the wine. A well-made wine at this time should be perfectly bright and all solid matters consisting of yeast, bacteria, and coagulated proteins should have accumulated in the sediment.

Racking should take place when possible only in settled weather, when the barometric pressure is high. Low atmospheric pressures diminish the solubility of the carbon dioxide with which the wine is saturated. Under these conditions, therefore, bubbles of gas are apt to be given off, bringing up particles of sediment and rendering the wine cloudy. However long wine is kept in wooden casks, it will continue to deposit sediment owing to chemical changes due to the action

of oxygen which penetrates slowly through the wood. Repeated rackings are therefore necessary, at least twice a year until the wine is bottled or consumed.

Abundant aeration is required during active fermentation; a more moderate supply of oxygen is important later for the proper ageing of the wine. Experience has shown that exactly the requisite amount of pure filtered air for the latter purpose will obtain access to the wine through the pores of the wood of ordinary oak casks of proper size. If the casks are too small the oxidation will be too rapid, if too large the maturing of the wine will be unduly prolonged. The temperature of the storage cellar is a modifying factor. The warmer the cellar the larger the casks should be.

With sound, completely fermented wines, all aeration, other than that due to the porosity of the wood, should be avoided as much as possible. This is accomplished by keeping the casks tightly bunged and completely filled. Evaporation through the wood continually diminishes the volume of wine and the lack must be supplied by filling up, at first two or three times a month and later every month or two. The drier the air of the cellar, the more frequent the fillings neccessary.

A light sulphuring of the clean casks into which the wine is racked is usual. This should be practiced with great caution. Very little is needed with sound wines, especially if sulphuring has been used also before or during fermentation. A slight excess will injure the flavor, and the amount should not exceed 2 gm. per hectoliter, while one-half to one-third of this is sufficient for old wines. The amount can be accurately measured only when using metabisulphite or the liquefied gas.

All the manipulation of the wine should be conducted with strict attention to cleanliness. This applies especially to empty casks, pumps, and hoses. These should be thoroughly cleaned immediately after use and, if made of metal or of other non-absorbent material, should be kept perfectly dry. Utensils of rubber, wood, or other porous material should be preserved from bacterial or mold growth with sulphurous acid.

The clarification, or fining, of a perfectly sound wine may be facilitated and hastened by thorough stirring of the yeast immediately before racking. The yeast in settling carries down much of the finer suspended matter, thus effecting a rough fining. Materials such as kaolin, pure silica sand, charcoal, and filter paper can be used with the same effect. The fining, however, is never perfect and the flavor of the wine is often injured.

The best wines are nearly always fined at least once, immediately before bottling. One or two finings may precede this to hasten ageing, defecation, and bottle ripeness.

The materials used for fining are soluble gelatinous or albuminous substances which are capable of being coagulated and precipitated by some ingredient of the wine. The best of the commonly used substances are isinglass (ichthyocol) 2 or 3 gm. per hectoliter, the white of fresh eggs, 1 or 2 per hectoliter, and gelatin, 10 or 12 gm. per hectoliter.

The proper quantity of the finings is dissolved in a little water diluted with wine and stirred into the cask. Acids (in grape wine, tannin, etc.), of the wine cause a gradual coagulation in minute particles throughout the liquid. These particles gradually coalesce, forming larger particles which include all the other floating solid matter of the wine as in a net. These larger particles contracted by the alcohol then settle to the bottom, leaving the wine bright.

The amount required varies with the quality of the fining agents used and the composition and temperature of the wine.

To precipitate commercial gelatin of good quality about an equal quantity of good tannin is necessary; therefore if the tannin is insufficient, as in citrus wines, it must be added; isinglass properly prepared requires only from one-half to one-third this amount; egg-white requires only minute quantities.

Specially prepared casein of milk is sometimes used for fining wine. Its chief merit is that the acids of the wine suffice to cause its complete precipitation and no addition of tannin is needed. Many other albuminous substances such as milk, blood, and various proprietary preparations are also used, but are all inferior to these mentioned and many of them introduce foreign matters, such as milk sugar and bacteria, which are a source of danger to the wine.

Wines containing many wine disease-producing bacteria may be injured by the introduction of finings. The evolution of gases due to the bacterial action may prevent the settling and the protein matter introduced will favor the multiplication of the wine disease organisms. By the use of 5 to 10 gm. of sulphurous acid per hectoliter added to the wine immediately before the addition of the gelatin, the bacteria with the other floating particles are precipitated.

The bright wine should be racked from the finings very soon after the sediment has settled, especially when its disease-producing bacteria are numerous. This will be in from ten to twenty days. If the wine is not clear in three weeks it should be filtered.

Filtering is inferior to fining in producing a perfectly bright wine. It is more rapid, however, and is useful in clearing wine refractory to fining.

Filters of innumerable forms are used. They are of two main types. For rough clearing of very cloudy wines some form of bag filter is usually employed in which the wine passes through a cloth tissue. The passage is rapid at first and the filtration imperfect. As the solid matter accumulates on the filtering surface, the filtration improves but the passage of the wine is retarded. The first wine is passed a second time through the filter but as soon as the rate of filtration becomes too slow the operation must be stopped and the filtering surface removed.

For wines containing little sediment the filter must be "primed." This is accomplished by putting some finings in the wine first passed through the filter. The priming is more effective and the output of the filter much increased if a little infusorial earth is used with the gelatin.

For the more perfect clearing of old wines from which it may be desired to make vinegar some form of pulp filter is used. There are various devices by which the wine is forced through a mass of cellulose or asbestos pulp and freed from all floating matter. Some of the best of these, carefully used, remove nearly all of the bacteria present.

Wine that cannot be assured of storage in a cool place should be pasteurized, unless it contains sufficient alcohol to protect it against spoiling by bacterial fermentation. A pasteurization temperature of 140°–150°F. is usually sufficient.

ANALYSES OF COMMERCIAL ORANGE WINE

Samples of beverages bearing the name of orange wines examined at the Enology Laboratory of the University of California all proved to be sweet liquors with medium to high alcoholic content and with a flavor of orange extract or orange oil. They gave evidence of having been made from sherry, sweetened by the addition of sugar and flavored by the addition of orange extract or oil in some cases, and in others of having been made from poorly fermented orange juice fortified by the addition of alcohol and sweetened by large additions of sugar. Analyses of such "wines" are given in Table XX.

Sample 3 was evidently a sherry flavored with orange oil or extract and sweetened. Nos. 1 and 2 may have been partially fermented orange juice that had started to turn to vinegar and had been then fortified by the addition of alcohol or brandy and sweetened by the addition of sugar or syrup. These were all "liquors" of bad quality and mislabeled, as their composition and flavor showed that they had no right to the title "Orange Wine."

TABLE XX

ANALYSES OF "ORANGE WINES"

Sample	Alcohol (Per Cent)	Total Acid	Volatile Acid (Per Cent)	Total Sugar (Per Cent)
1	9.6	....	.47	21.6
2	9.6	....	.26	18.9
3	18.0	....	.08	17.6

TABLE XXI

ANALYSES OF ORANGE WINES MADE IN THE LABORATORY

Sample	Alcohol (Per Cent)	Total Acid (Per Cent)
1	4.25	1.5
2	4.5	1.52

Neither of these wines gave any perceptible taste of sugar. Both were very low in alcohol as compared with the artificial orange liquors cited in Table XX. The acid in the true orange wines is very much higher than that in the artificial product. Some of the wines were made in the laboratory by treating the fresh juice with potassium metabisulphite at the rate of 4–6 oz. per 100 gal. and allowing the juice to settle until clear. Pure yeast was added to the clear juice after drawing it off the sediment. Another lot of the juice was allowed to ferment naturally. Both lots of wine were filtered after fermentation. Neither gave any trouble and both gave a brilliantly clear wine.

SPARKLING WINES

In some countries the filtered wine is made into sparkling wine as follows, after the first fermentation is over. To the filtered wine is added 1.5 per cent cane sugar previously made into a thick syrup and boiled with a little citric acid. This would be about 1.8 oz. of sugar per gallon of wine. To this, a little champagne yeast is added and the wine bottled in champagne bottles. The bottles are corked with champagne corks and left in a warm place for a few days until fermentation starts in the bottles. The corks must fit very tightly and must be well tied down. During the first few weeks, the bottles should be turned often to prevent the yeast from sticking to the sides of the bottles. They are then placed in a cool place until fermentation in the bottle is complete after which they are turned cork downward for several months. The yeast sediment settles out on the cork. To remove this the bottle is then held in a slanting position and the cork released by cutting the string that holds it. The cork is shot out of the bottle by the gas pressure within and carries the yeast

sediment with it. It must be replaced quickly by a new cork, before too much gas escapes or before too much of the wine is lost.

A sparkling orange wine made in the Zymology Laboratory of the University of California, though not relieved of its yeast sediment as described above was pronounced preferable to the still wine made from the same juice.[1]

PARTIALLY FERMENTED JUICE AS A BEVERAGE

One of the most satisfactory processes for securing a pleasant drink from orange juice is that in which fermentation (with a special yeast) is allowed to proceed for only a very short time in order to keep the alcohol percentage within the legal limit after which the juice is pasteurized. The result is a sweet, light, sparkling juice even after seven months' storage.

ORANGE VINEGAR

Nature and origin of vinegar.—Vinegar is made from various sugary or starchy matters by alcoholic and subsequent acetic fermentation. It should contain from 4 to 8 per cent of acetic acid and natural flavoring, coloring, and other matters varying according to its origin.

Theoretically, 1 per cent of alcohol converted into acetic acid will yield 1.2 per cent of the latter. Actually, 1 per cent of alcohol gives approximately 1 per cent of acetic acid. Therefore orange juice of 11 per cent sugar, yielding alcohol of 5.5 per cent, should give vinegar containing considerably over the minimum legal limit of 4 per cent acetic acid.

Fermentation.—The transformation of the alcohol of the fermented orange juice into acetic acid takes place only with an abundant supply of air because it consists in the addition of the oxygen of the air to the alcohol, in this way changing it into acetic acid or vinegar.

The quality of the vinegar will depend on the quality of the raw material from which it is made. Wine spoiled by bacterial fermentation, moldy casks, etc., will make inferior vinegar. The wine should be perfectly clear and clean tasting and, if necessary, should be fined, filtered, or pasteurized immediately before use. It should contain no antiseptic which would interfere with the development of the acetic bacteria. Sulphurous acid is particularly troublesome in this respect, and should be removed or oxidized by thorough aeration.

Before starting the acetic fermentation, it is a usual and good practice to add about 10 per cent of good vinegar to the liquid, which is thus rendered acid and therefore less liable to alteration by injurious bacteria and other micro-organisms.

[1] 1914.

All the processes of vinegar-making depend on the same principle, which is to expose the wine prepared as above to the action of acetic bacteria with full access of atmospheric oxygen at a suitable temperature. The rapidity of the process depends on the number of active bacteria present, the nutritive value of the liquid, the temperature, and especially the free access of oxygen.

a) *Starters and pure cultures.*—The 10 per cent of vinegar added to the liquid to be fermented usually contains sufficient bacteria to insure a prompt start. Where this is not the case, a starter may be prepared by exposing a suitable liquid in a shallow vessel to the air of a warm room for several days. Any liquid containing about 4 per cent of alcohol, 2 per cent of acetic acid, and a moderate amount of nitrogenous matter is suitable. A decoction made by boiling 50 gm. of fresh yeast in 1,000 c.c. of water, filtering, and adding the proper amount of vinegar and wine will serve. After thorough aeration, such a liquid in a few days becomes covered with a film of acetic bacteria. This film may be used as a starter by gently submerging the vessel in which it is formed in the liquid to be acetified, or by removing with a clean sliver of wood which is afterward floated in the liquid.

In practice, such a starter gives a sufficiently pure fermentation of acetic bacteria. The particular species of acetic bacteria, however, is left to chance. Pure cultures of a special selected form would in all probability improve the certainty of the production of good vinegar, but the method has not entered into general practice.

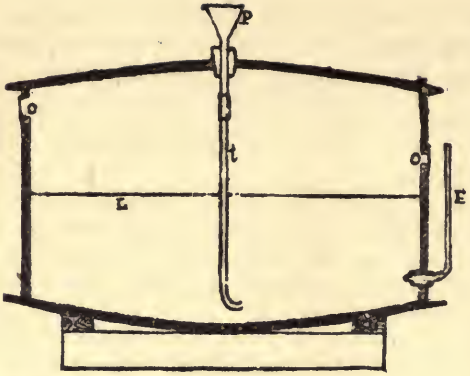
b) *Apparatus.*—Most metals of all kinds should be avoided as much as possible. The hoops of barrels and buckets may be protected by a coating of paraffin. Pumps may be of wood or of special non-corrosive alloys, or they may be so constructed that they will not come in contact with the liquids.

c) *Domestic method.*—A cask of convenient size (40 to 200 liters) is fitted as illustrated in Figure 14.

The wine to be acetified is poured, after filtering, if necessary, into the cask until it is about one-half to two-thirds full, the object being to have as large a surface as possible for the growth of the bacterial film. Free circulation of air is insured by a 5-cm. hole in each head of the cask, one near the surface of the liquid and one near the top of the cask. These holes should be covered with varnished metal netting to prevent the entrance of flies.

The top bung hole is then closed with a cork, through which a funnel passes, furnished at its lower end with a glass or rubber tube extending to within a few inches of the bottom of the cask. By means of this funnel new liquid can be added without disturbing the surface film. The lower bung hole is closed with a cork, through which passes an L-shaped glass tube which serves as an indicator of level and which also can be used to draw off the vinegar.

When this apparatus is working well, one-fifth to one-quarter of the contents may be taken off every three or four weeks. This depends on the temperature, which should be between 10° and 18°C. The vinegar



(*Bioletti in Marshall: Microbiology*)

FIG. 14.—Vinegar barrel. *L*, surface of liquid; *O*, *O*, openings for entrance of air; *t*, tube for introducing new supplies of wine without disturbing surface films; *E*, glass tube to show level of liquid and for drawing off vinegar.

drawn off is immediately replaced with wine which, if added slowly, will, owing to its lower specific gravity, remain at the surface in contact with the bacterial film.

d) Orleans method.—This is practically the same as the method just described with slight modifications to adapt it to large-scale operations. It is the oldest commercial method and produces vinegar of the highest quality.

Barrels of about two hectoliters are usually employed, fitted essentially like that already described but with the omission of the funnel and drawing-off tubes.

The wine is first cleared in a vinegar filter. This consists of a wooden vat filled with beech chips which have been extracted by soaking for several days in cold water. The wine remaining in contact with these chips for three or four days deposits most of its sediment.

The cask is first one-third filled with good vinegar and ten or fifteen liters of the filtered wine added. The same amount of wine is added every week for four weeks by which time the cask is half full. At the end of the fifth week an amount of vinegar equal to the wine added is drawn off and the operation repeated. The vinegar is filtered as soon as it is drawn off, placed in full, tightly bunged casks and kept in a cool cellar.

e) Pasteur method.—Pasteur long ago pointed out the defects of the old Orleans method and suggested improvements. The main defects of the old method are that it is cumbersome, laborious, slow, and costly. There is a loss of about 10 per cent of material by evaporation and the repeated additions of liquid break the bacterial film, which then sinks to the bottom, grows anaerobically, and exhausts the nutrients of the solution without producing acetic acid. These submerged bacteria finally form a large gelatinous mass which interferes with the regular progress of the operations, depreciates the quality, and necessitates frequent expensive cleanings of the casks. Many attempts, more or less successful, to overcome these defects in accordance with Pasteur's ideas have been made, but that of Claudon is one of the best and will serve to exemplify all.

It requires the use of a wide, shallow, covered square vat, furnished with numerous openings near the top by which the entrance of air can be facilitated and regulated. This vat is filled to the bottom of the air vents with a mixture of four parts of good new vinegar and six parts of wine which has been pasteurized at 55° and, when necessary, filtered. On top of this liquid is floated a light wooden grating which helps to support the bacterial film and prevent its breaking and submerging during the various

operations. When the vat is filled, the process is started by placing a small quantity of a good bacterial film on top of the liquid which soon becomes completely covered when the proper conditions of temperature and aeration are maintained.

Each acetifying vat is connected with a small measuring vat from which the proper amount of liquid is added every day after a corresponding amount of vinegar has been removed. These two vats constitute a unit, several of which, usually six, are united in a battery. A factory includes several of these batteries.

The batteries are fed from a large vat or reservoir, where the mixture of wine and vinegar is prepared and stored. The vinegar drawn from the batteries runs directly to filters, thence to a pasteurizer, and finally to the storage casks.

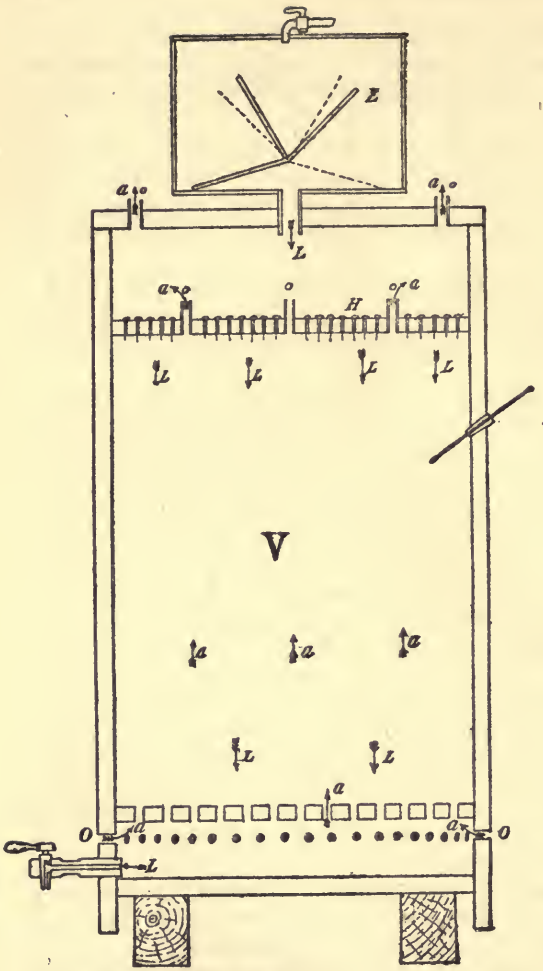
The output of these batteries is from two to five times as great per square meter of acetifying surface as that of the old method; the cost of the operation is considerably less, the loss by evaporation much reduced and the quality equal and much more under control of the manufacturer.

f) *German method.*—In all the methods described, the surface of the liquid exposed to air, where alone acetification occurs, is small compared to the volume of the liquid. In order to hasten and therefore cheapen the process, various devices for increasing the surface in contact with air have been designed. The simplest of these is one sometimes employed in wine-making countries. The present pomace from wine is broken up and placed loosely but uniformly in a tall, narrow vat. In a few days, acetic fermentation commences in all parts of the mass. Wine is then sprinkled periodically on top, and, trickling down over the pomace, it is changed to vinegar by the bacterial film which incases every particle of the mass. The "quick" or German method of vinegar-making is based on this principle.

The apparatus used in this method consists of a tall cylindrical or slightly conical wooden vat provided with a perforated false head a few inches from the bottom and another, similar in structure, at the same distance from the top. The space between these two false heads is filled with long thin chips or shavings of beech wood which have been thoroughly extracted, first with water and then with good, strong vinegar.

In operation, the liquid to be acetified is distributed over the top false head intermittently in small amounts. This intermittent supply is accomplished by various automatic devices. If the supply is continuous, the liquid tends to run in streams or currents in certain parts of the vat and much of the acetifying surface is lost; if too rapid, the bacterial film is removed from the upper part of the mass of beech chips and only the lower part is effective.

From the false head, the liquid passes through numerous small holes to the mass of beech chips, over which it trickles slowly and is acetified by means of the bacterial film which covers them. By the time it reaches the lower false head, the alcohol is in greater or less amount converted into acetic acid. Usually the liquid must pass through from two to five times or through an equal number of vats before it is completely changed into vinegar. The number of passages depends on the amount of alcohol pres-



(*Bioletti in Marshall: Microbiology*)

FIG. 15.—Rapid process vinegar apparatus. *V*, mass of beech chips over which the alcoholic liquids run from *H*; *H*, false head with numerous small holes and threads for the slow and equal distribution of the liquid; *E*, filtering trough for the intermittent supply of liquid; *O*, opening for the entrance and exit of air.

↑ path of air. ↓ path of liquid.

ent, the height of the acetifying column, the rapidity of the flow, the temperature, and on the perfection of the apparatus.

Oxygen is supplied by the air which, entering holes in the vat below the lower false head, passes through numerous holes in the latter, through the interstices between the chips and out through short tubes fixed in the upper false head and holes in the top. The passage of air is insured by the heating of the interior due to the fermentation. It can be regulated by the number and diameter of the air holes.

The temperature, which should be close to 30°, must be carefully regulated. If the temperature rises too much, the loss by evaporation will be greatly increased; if it remains too low the acetification will be retarded.

Many modifications of this method exist, having principally for their objects the more complete regulation of the temperature and air supply, recovery of the volatile matters and avoidance of the need of repassing the liquid through different acetifying columns.

g) *Rotating barrels.*—Several methods are in use which attempt to combine the rapidity of the German machines with the quality of the Orleans method. Wine and cider cannot be acetified conveniently by the German method on account of the large amount of solids and extractive matter they contain. This coats the beech chips rapidly and interferes with the perfect working of the process.

These methods make use of a barrel filled partially or wholly with beech chips and half-filled with the liquid to be acetified. By rotating the barrel at short intervals the liquid trickles repeatedly over the chips and with proper aeration, the acetification is rapid and complete.

After-treatment.—Wine (and cider) vinegars, for the best results, require ageing and careful treatment. They should be filtered and pasteurized as soon as made and stored in clean casks which are well bunged and kept constantly full in a cool place of even temperature. If too dark in color they may be decolorized with pure animal charcoal carefully extracted with acids and water.

Before using or bottling, the vinegar should be fined with isinglass.

The results obtained from the juice made into vinegar by yeast fermentation followed by vinegar fermentation brought about by the addition of strong vinegar equal in volume to one-fourth the volume of the fermented juice, are given in Table XXII.

TABLE XXII

YIELDS OF ACETIC ACID IN ORANGE VINEGAR FROM FROZEN ORANGES

Sample	Balling Per Cent of Original Juice	Total Acid in Vinegar	Volatile Acid (Vinegar Acid) in Vinegar	Alcohol in Vinegar
1. 717*d*	12.2	6.44	5.18	Trace
2. 717*e*	12.5	4.36	3.36	Trace
3. 717*f*	12.5	4.80	3.60	Trace

The juice for sample 1 was defecated with the help of sulphurous acid and the clear juice was fermented with pure yeast. The clear wine was allowed to stand several days after alcoholic fermentation and was then drawn off the yeast and fermented into vinegar by use of a vinegar starter. The juice for samples 2 and 3 was made from the same oranges as that of sample 1. This juice was divided into two equal portions. Neither received any sulphurous acid or defecation and both were fermented with pure yeast. The wine of sample 2 was drawn off the yeast and acetic fermentation carried out as in sample 1. Sample 3 was treated in the same manner as sample 2 except that the wine was not drawn off the yeast and sediment before acetic fermentation.

Most of the orange flavor was lost during vinegar fermentation and the flavor of the finished vinegars was not so agreeable as that of apple or wine vinegar. The inclusion of a little of the orange oil from the skins during extraction of the juice might improve the flavor, or at least increase the orange flavor.

Diseases.—The most troublesome pest of vinegar factories is a minute nematode, the *Anguillula aceti* or vinegar eel. It often develops around the edges of the surface of the liquid in vinegar barrels and in the acetifying columns and, if neglected, may cause putrefaction and spoiling of the vinegar. Frequent and thorough cleaning of all apparatus, pasteurization

of liquids, and light sulphuring of empty casks will prevent its development.

Microscopic mites are sometimes troublesome in neglected factories. They can be reduced by the methods recommended for vinegar eels and their entrance into the barrels or acetifying columns prevented by painting a ring of turpentine or some viscid substance around each air hole.

Vinegar flies (*Drosophila cellaris*) are often troublesome, but can be excluded by proper screening of buildings and barrels.

Bacteria other than acetic may develop in vinegar and some of them may depreciate its quality. These have been little studied but the most harmful seem to be anaerobic forms which develop in the lower parts of the liquid protected from oxygen by the screening film of the acetic bacteria. They produce butyric acid and putrid odors and, if neglected, may completely spoil the vinegar. Sulphuring, fining, and pasteurization are the remedies.

Darkening or persistent cloudiness may be caused by oxidase as in wine and cider and is controlled in the same way. A similar defect may be caused by the tannic extractive matters of new casks or contact with iron. Aeration followed by fining will remove the cause of the trouble.

ACETONE

Cruess has suggested the possibility of making acetone as a citrus by-product. Acetone is obtained by the neutralization of acetic acid with calcium carbonate or oxide followed by dry distillation of the calcium acetate. During distillation the calcium acetate decomposes to form calcium carbonate and acetone, the acetone distilling over. By this process 1 gal. of alcohol when passed through the processes of acetification, neutralization, and dry distillation will yield not more than .6 gal. of acetone. One ton oranges = 6 gal of absolute alcohol = 3½ gal. acetone at $2.25 per gal. = $7.85 per ton of oranges. The manufacture of acetone from oranges appears to be a more attractive possibility than the manufacture of alcohol.

The manufacture of acetone, like many other fermentation processes, requires a large number of fermentation vats for alcoholic fermentation, large crushers, pressers, many acetic acid or vinegar generators, and a still. It is desirable to distil the alcohol from the fermented juice before acetifying because this facilitates working of the generators, gives a purer acetic acid, and permits the recovery of the citric acid, a very important consideration.

The total value of a ton of oranges for acetone, citric acid, and oil would be about $18.85 to $20.85.

CITRIC ACID FROM LEMONS

Citric acid, as its name implies, occurs principally in the juice of the citrus fruits and is chiefly responsible for the sour taste of these fruits.

Commercially it is derived mainly from the juice of the lemon, although smaller amounts are obtained from the lime, bergamot, and orange. Citric acid is usually made from the inferior fruit or "cull lemons" which have been damaged by insects, fungi, or frost, or which are misshapen, undersized or even oversized. It may be regarded, therefore, as a by-product of the lemon-growing industry.

The principal use of citric acid is in the manufacture of beverages and effervescent salts. It is also used in the manufacture of many salts which are used in medicine, including the citrates of ammonium, bismuth, caffeine, iron, lithium, magnesium, potassium, quinine, and sodium. Citric acid and sodium citrate find some application in textile printing and in the manufacture of a few dyes. Many formulas for photographic developers and toning baths contain citric acid or sodium citrate. Ferric ammonium citrate is used in the manufacture of blueprint paper. Citric acid and ammonium citrate are important laboratory reagents. They are essential for the determination of phosphates in fertilizers, which ranks as one of the most important of analytical operations.

From 8,000 lemons, pressed in a suitable press, 700 liters of juice, containing 4.5 to 6 per cent of citric acid are obtained. Fresh lemon juice contains also 7 to 9 per cent of glucose, 0.2 to 9.8 per cent of saccharose (according as the lemons are sour or ripe), certain extractive, gummy, and pectic substances (about 0.2 per cent for ripe and 0.8 per cent for unripe fruit), and about 0.5 to 0.7 per cent of inorganic salts. The presence of these substances renders it impossible to crystallize the citric acid merely by concentrating the juice, even when all the glucose is transformed into alcohol (5 to 6 per cent), so that, even at the present time, the citric acid is separated by Scheele's classical and rather costly process, according to which it is first converted into calcium citrate.[1]

The high price of fuel has prevented the establishment of the citric acid industry in Sicily, and the preparation of the acid has been monopolized for a long time by England and, at the present time, largely by Germany. Both these countries receive the raw material from Sicily, to a small extent as lemons packed in barrels containing sea water, partly as concentrated juice (agro cotto), but mostly as calcium citrate.

In consequence of the development of lemon-growing in Spain, and especially in California and Australia, and also owing to an agreement entered into by the manufacturers of citric acid, the condition of the Sicilian growers became so critical that in 1903 the Italian Minister of Agriculture offered a prize of £6,000 for improvements in the industry or new processes of value to the cultivators. This sum was largely wasted

[1]For a method covering the manufacture of citric acid from impure calcium salts see H. Tobler, United States Patent No. 1288293, December 17, 1918.

by commissions who achieved nothing, or by rewarding certain favored individuals. However, at the end of 1904, Professor Restuccia, of Messina, announced to the government the discovery of a process for the direct extraction of citric acid by simple concentration of the juice, to which was previously added a trace of a substance—the nature of which he did not reveal (picric acid)—and a little animal charcoal, but this process only led to further waste of money.

In 1910, Peratoner and Scarlata suggested the following new process for extracting the essence and citric acid from the lemons directly, without a conversion of the acid into the calcium salt. The juice obtained by squeezing the minced lemons in hydraulic presses is partly distilled in a vacuum on a water bath at 60° to recover the essence and then concentrated *in vacuo* at 70° until it acquires a syrup consistency (one-tenth of the original weight). When the syrup is cold, all the citric acid is extracted by treatment with a mixture of alcohol and ether, in which many of the impurities are insoluble. The alcohol and ether are recovered by distillation, and the residue diluted with a little water, filtered, and concentrated *in vacuo;* after standing for twelve to twenty-four hours it sets to a yellowish-red crystalline mass which, after defecation and decolorization in the ordinary way (animal charcoal, etc.), gives pure colorless crystals, the yield being 60 to 70 per cent. The remaining acid may be separated from the mother-liquor as citrate.

In spite of the favorable opinion expressed by Professors Garelli and Paterno, this process does not seem to have been applied practically.[1]

Meanwhile the crisis in Sicilian citrus industry, which had apparently lessened as a result of the good crops and prices of 1906 and 1907, became aggravated in 1908 owing to the diminished demand for lemons, the American financial crisis, and the agreement between the producers of citric acid to limit the amount of raw material required—thus lowering prices and exhausting the usual stock of treated products—and finally, to the abundant production, since refuse lemons did not sell for enough in 1908 to pay for gathering.

Various measures have been taken by the Italian government to protect the citric acid industry in Sicily, but it should be possible in the present advanced condition of technical chemistry to develop this industry without such aid. The sulphuric acid required is now made in Sicily itself, and by the use of a multiple-effect evaporating plant, the consumption of coal may be reduced to a minimum. In 1911 a large citric acid factory was erected in the vicinity of Palermo by the firm of Goldenberg, of Winckel, near Wiesbaden.

[1]Poore made (1923) experiments using collodion sacs in dialyzing lemon juice, followed by dialysis on a large scale in an osmogene containing colodion-impregnated cloth membrane, giving the following results: (1) The small quantity of colloids present in lemon juice does not affect crystallization, but the ash and other non-acid constituents prevent satisfactory crystallization of concentrated fermented juice. (2) In the presence of ash and other impurities, needle and leaflet modifications of citric acid crystals are obtained; upon the removal of half of the ash, characteristic citric acid crystals are formed. (3) At the concentration necessary for crystallization, the mother-liquor is so viscous that the crystals cannot be separated.

In the large modern Sicilian factories, the juice is treated in almost the same manner as in the manufacture of tartaric acid: into 100-hectoliter masonry vessels provided with stirrers and cold-water coils are placed 20 hectoliters of concentrated juice and 80 hectoliters of water, the liquid then being well mixed for thirty minutes and allowed to ferment, the glucose thus converted into alcohol and the juice clarified. By passing very cold water through the coil, the temperature of the liquid is lowered to 5°, and a large part of the dissolved and suspended extractive and mucilaginous matters separated; in presence of a little tannin, these matters coagulate and do not redissolve (50 liters of sumach extract at 10° Bé. are sufficient, the liquid being stirred for fifteen to twenty minutes immediately after the addition). The solution is then passed by the filter presses and thence into 20-hectoliter wooden vats or into brickwork vessels similar to the preceding ones, but provided with perforated coils for direct-steam heating. The boiling liquid is now neutralized exactly with dense milk of lime or with powdered calcium carbonate. The latter causes frothing and sometimes overflow of the liquid, but precipitates a purer calcium citrate, while the hydroxide throws down many pectic and coloring matters. In some cases two-thirds of the acidity is neutralized with calcium hydroxide and the remainder by the carbonate. For every 100 kilos of citric acid present (titrated) 45 kilos of quicklime (57 of slaked lime per 80 of the carbonate) are added. After stirring while hot, the insoluble tricalcic citrate—which forms immediately—is passed at once through the filter presses and washed for ten minutes with very hot water, for ten minutes with tepid water, and for five minutes with cold water, which should remain almost colorless. In other parts of Sicily, calcium citrate is prepared in a primitive method (with slaked lime often containing magnesia, which yields soluble magnesium citrate, this being lost) and is sold dry with a content of 64 per cent of citric acid. Three hundred kilos of calcium citrate of this strength require, on the average, 100,000 lemons, the peel of which yields 37 kilos of essence, selling at $1.52 per kilo. The total cost of manufacturing calcium citrate and essence from 100,000 lemons was, before the war, about $48.60. The cakes of calcium citrate from the filter presses are mixed in 20-hectoliter lead-lined vessels with 15 hectoliters of cold water, the lime of the citrate being then neutralized exactly with dilute sulphuric acid (1 : 5) (with 100 kilos of citric acid in the juice correspond 400 kilos of this dilute acid); a slight excess of sulphuric acid is always added, since the presence of unaltered calcium citrate would hinder the crystallization of the acid.

The acid is added in portions at the rate of 5 liters per minute, the liquid being kept well mixed and direct steam applied through a perforated leaden coil. The mass is boiled for ten to fifteen minutes, the steam being then suspended and the whole mixed for thirty minutes. The calcium sulphate is then removed by means of a filter press and is washed with 200 liters of boiling water, which is added to the first filtrate, and then with cold water, which is afterward used for treating fresh calcium citrate. The citric acid solutions from the filter presses contain only minimal quantities of sulphuric acid and certain blackish extractive matters. Concentration of the solution was formerly carried out in lead-lined wooden vessels,

4 m. long, 2 m. wide, and 25 cm. deep, containing closed steam coils. Evaporation should be rapid and the temperature should never exceed 65° to 70°. When the liquid reaches 46° (specific gravity 1.3), almost all the calcium sulphate previously remaining in solution separates; the clear liquid is then siphoned into a similar vessel underneath, the concentration being continued until a crystalline skin forms at the surface of the liquid, which is next transferred to wooden crystallizing vessels, 2 m. × 70 cm. × 20 cm. (deep); the inner surface is polished with plumbago. After two days, the dark-brown mother-liquors are removed and the yellowish-brown crystals centrifuged. In order to separate traces of dissolved iron from the mother-liquor, this is treated with a little potassium ferrocyanide and filtered; two or three further crops of dark-colored crystals are obtained, the very dark mother-liquor finally obtained being added to fresh lemon juice.

In modern factories the citric acid solution, freed from calcium sulphate by filter-pressing, is concentrated in vacuum apparatus, just as in the sugar and tartaric acid industries, the density 45° to 50° Bé. in the hot being attained. In this way the temperature does not exceed 60° to 65°, and with a triple-effect apparatus not only rapidity, but also economy of fuel, is attained.

In order to remove the calcium sulphate remaining in solution, the concentration is effected in two phases: in the first to 26° to 28° Bé., the liquid being then cooled in suitable vessels in which the gypsum deposits; the residual liquid is then concentrated further to 48° to 50° Bé. This liquid is discharged into the crystallizing vessels, which are of lead-lined wood and of large surface; the mother-liquors are reconcentrated and recrystallized two or three times, and are finally worked up to crude calcium citrate. The blocks of crystals left in the crystallizing vessels are broken up with wooden mallets and centrifuged.

The brown crystals first obtained are refined and decolorized by dissolving them in rather more than double their weight of water (to a solution of 20° Bé.) and boiling the solution with animal charcoal previously treated with hydrochloric acid, as in the refining of tartaric acid.

The hot liquor is filter-pressed under low pressure until it becomes clear and free from particles of charcoal. The filtrate is concentrated in a vacuum at about 60° to 65° until crystals of citric acid form, and is then heated to 90° and discharged into lead-lined crystallizing vessels, in which it is stirred at intervals so as to obtain small crystals; after forty-eight hours these are centrifuged and washed in the centrifuge with pure citric acid solution, just as is done with sugar.

If chemically pure citric acid free from metals is required, the concentration is carried out in thickly tinned vessels and the crystallization in wooden vessels; the traces of iron present are eliminated by addition of a little potassium ferrocyanide and sodium sulphide.

In all the washing and refining operations, pure water with little hardness is always employed.

OTHER SOURCES OF CITRIC ACID

CITRIC ACID BY FERMENTATION

Five different species of fungi, namely, *Citromyces Pfefferianus, Citromyces glauber, Mucor piriformis, Citromyces citricus,* and *Sterigmatocystis nigra,* have been shown to produce citric acid by fermentation but comparatively little work has been done by the experimenters to find the value of this formation, while up to the present time only one firm in America has found it of commercial value.

From a review of the literature on the subject the general conditions for this fermentation are: A neutral slightly acid solution containing proper nutrient salts and dextrose, not exceeding 10 per cent. (However, the fungi are not dependent on this form of sugar alone, for sucrose, lactose, mannose, xylose, arabinose, glycerol, and alcohol all produce citric acid.) The temperature should be carefully regulated.

The citric acid fermentation induced by certain fungi has been elaborately studied, especially by Wehmer. His work on this subject and also on the oxalic acid fermentation is familiar to all students of fungi. Wehmer believed that the production of citric acid in more than mere traces was characteristic of the group of fungi to which he gave the generic name *Citromyces* and that oxalic acid fermentation was characteristic of *Aspergillus niger.* This seems to have been accepted by all the other workers who have investigated either the citric or oxalic acid fermentation. Martin, in a study of the citric acid fermentation, discarded all cultures of *Aspergilli* with the assumption that their fermentative action was well known and that they did not produce citric acid.

It has been noted[1] that many cultures of *Aspergillus niger* produced citric acid. Although the literature on the chemical activity of *Aspergillus niger* is voluminous, only one reference has been found relative to citric acid production by this mold. In 1913 Zahorski was granted a patent in the United States on a method for producing citric acid by fermenting sugar solutions with *Sterigmatocystis nigra.* This is one of the many names that have been used to designate fungi of the black *Aspergillus* group. Zahorski, however, states that *Sterigmatocystis* differs distinctly from *Aspergillus.*

Currie at first supposed that Zahorski had worked with some very unusual culture of *Aspergillus niger.* This impression was probably wrong, for any one of about twenty cultures studied under certain conditions produced citric acid in abundance. In fact almost any culture of *Aspergillus niger* upon concentrated sugar solutions will produce much more citric acid than oxalic acid. For conducting the citric acid fermentation a well-selected culture of *Aspergillus niger* is far superior to any culture resembling Wehmer's *Citromyces* with which Currie worked.

No cultures produced citric acid only under all conditions or oxalic acid only under all conditions.

Many of the workers who have studied the citric acid fermentation performed only a few experiments without being guided by a fundamental knowledge of the metabolism of fungi or of the conditions favorable to the reaction with which they were concerned. Experiments conducted in

[1] *Journal of Agriculture Research,* VII (1916), 1.

this way are not likely to make a very definite contribution to any problem. In Currie's work three fundamental factors with regard to *Aspergillus niger* have been considered: (1) the inorganic salt requirements; (2) the general equation of metabolism; and (3) the reaction of the medium.

Few concise statements can be made concerning the metabolism of an organism capable of producing such a variety of chemical transformations as *Aspergillus niger*. What is true for one set of conditions may not be true for another set of conditions differing ever so little. The general equation for the metabolism of *Aspergillus niger* may be written in the following form:

carbohydrate → citric acid → oxalic acid → carbon dioxide → mycelium.

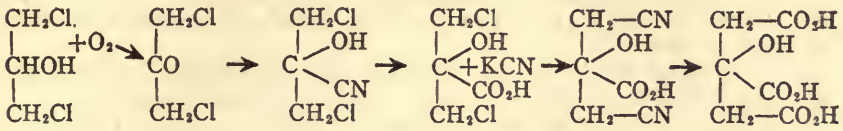
These four products are nearly always present. Although their proportions may vary widely with the culture employed and the conditions of growth, their sum will account for approximately 95 per cent of the consumed carbohydrate. By a judicious selection of cultures and conditions citric acid can be varied from none at all to over 50 per cent of the cane sugar consumed.

The conditions especially favorable to the citric acid fermentation are low nitrogen supply, high concentration of sugar, and nitrogen supplied as ammonium salts rather than as nitrates. Wehmer and also others who have studied the citric acid fermentation worked on the supposition that the acid should be neutralized as formed or the rise in acidity would interfere with the growth of mold. Oftentimes, therefore, calcium carbonate was introduced. However, in the limitation of the growth of fungi the hydrogen ion concentration of the media is of much more importance than their titrable acidity. The limiting pH for *Aspergillus niger* is about 1.6 and 1.4. Ten per cent of citric acid is equivalent to pH 1.6 and 20 per cent of citric acid to pH 1.4. After a concentration of 20 per cent citric acid is reached the increase in hydrogen ion concentration is very slight in comparison to the added acid. Consequently *Aspergillus niger* was found to make considerable growth on a medium containing 40 per cent citric acid. However, it is hardly practicable to consider producing a liquid containing more than 10 per cent citric acid, for the concentration of sugar required would exceed the point where fermentation proceeds most rapidly. It has been found that the addition of calcium carbonate caused in many cases contamination with foreign organisms which interfered with citric acid production. The growth of foreign organisms could be restricted by the addition of hydrochloric acid to a pH of about 3.5. Also the fermentation proceeded more rapidly in an acid medium than in one to which calcium carbonate had been added. There is also a possibility of recovering the citric acid directly from the fermented liquor, without going through the expensive process of separating and decomposing the calcium citrate. This cannot be done with lemon or lime juice because of the high percentage of sugar, pectin, and protein.

CITRIC ACID BY ARTIFICIAL SYNTHESIS

Citric acid can be obtained synthetically by a method evolved by Grimaux and Adam. A saturated solution of dichloracetonic acid is neu-

tralized with sodium carbonate, Na_2CO_3, and heated with two molecules of potassium cyanide, KCN. The resulting solution of dicyanoacetates is saturated with hydrochloric acid gas, HCl, and upon heating on a water bath for fifteen hours, the citric is then separated as calcium citrate by neutralizing with milk of lime.



More recently Lawrence has synthesized citric acid by decomposing ethyl citrate which had been formed by heating ethyl bromacetate and ethyl oxalylacetate in the presence of zinc.

Neither of these methods, however, has commercial importance at present but it must not be forgotten that artificial synthesis may sometimes result in furnishing dangerous competition for the natural product as is often the case in industrial chemistry.

ANALYSIS OF CITRIC ACID AND CITRATES

Citrate of lime.—The analysis of commercial calcium citrate (citrate of lime) is now generally carried out by Warington's method modified as follows:

Four gm. of citrate are boiled with 30 c.c. of 2N-hydrochloric acid in a 100-c.c. standard measuring flask for ten minutes, the solution being then cooled and made up to the mark with water. It is then shaken and filtered through a dry filter paper, 50 c.c. of the filtrate being measured by a standard pipette into a beaker of 300-c.c. capacity and exactly neutralized with dilute sodium hydroxide free from carbonate, using phenolphthalein as indicator. The solution is next made slightly acid by the addition of three or four drops of N-hydrochloric acid, 2 c.c. of a 45 per cent solution of calcium chloride added, the liquid raised to the boiling-point and kept boiling for fifteen minutes; to avoid bumping it is necessary to stir the liquid well until boiling, after which it can safely be left. The hot liquid is filtered and the precipitate on the filter paper washed with boiling water six times. The filtrate and washings are then made just alkaline by adding a drop or two of dilute ammonia, and boiled down to about 15 c.c. The precipitate which forms is collected on a small filter paper and washed with *boiling* water six times, using a very small quantity of water for each washing. The filtrate and washings are treated with a drop of ammonia, if they have become acid, and are boiled down to about 10 c.c., but as a rule no further precipitate will be obtained while the liquid is hot; any precipitate which forms on cooling can be neglected.

The filter papers with their precipitates are dried at 100° and burned together in a platinum dish with a cover. The flame should be kept low

until the whole is charred, and then gradually raised until the ash is white. The mass is then carefully treated with 30 c.c. of N-hydrochloric acid, and boiled until all is dissolved and all carbon dioxide expelled; the resulting solution is titrated with N/5 or N/2 sodium hydroxide, using phenolphthalein as indicator.

The sodium hydroxide is standardized by pure potassium hydrogen tartrate, and the N/1 hydrochloric acid by the alkali; phenolphthalein is used as indicator.

The number of c.c. of N/1 HCl used for the neutralization of the ash $\times$ 0.070 gives the weight of citric acid in the portion tested.

An almost identical method has been described by L. and J. Gadais.

If the citrate contains much sulphate it is advisable to ash at as low a temperature as possible, preferably with an alcohol flame. Before dissolving in hydrochloric acid, the ash should be treated with 10 c.c. of hydrogen peroxide. (If, as is usual, the hydrogen peroxide contains free acid, allowance must of course be made for it.)

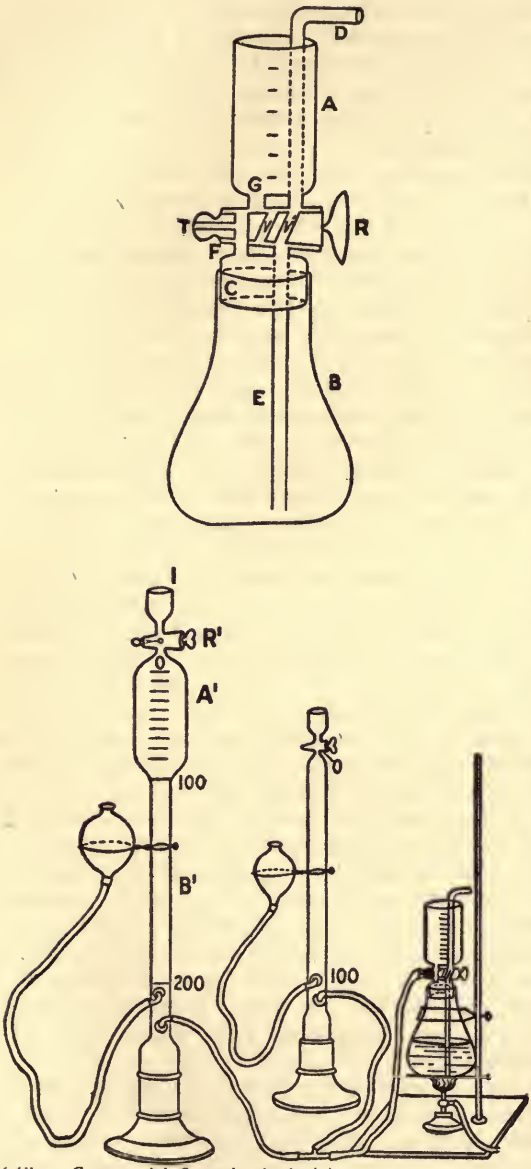
Lime juice, lemon juice, and factory citric acid liquors.—The analysis of these materials is conducted as follows: 15–20 c.c. of unconcentrated juice, or an amount corresponding with 3 c.c. of concentrated juice (40 gm. per 100 c.c.), previously diluted to facilitate exact measurement, are exactly neutralized with pure potassium hydroxide (N/5). The liquid, having a volume of about 50 c.c., is heated to boiling, mixed with a slight excess of concentrated calcium chloride solution, and kept at a gentle boil for half an hour. The precipitate is filtered off immediately while hot, washed with boiling water six times, and the mother-liquor and washings again evaporated and worked up as described above under calcium citrate. The whole of the calcium citrate collected is then dissolved in 30 c.c. of N/1 hydrochloric acid and the excess of acid estimated as above. In dealing with the cruder factory liquors three or four evaporatings are generally necessary to separate all the calcium citrate.

The foregoing methods are not entirely free from error (O. von Spindler) but have not yet been replaced by better. Incorrect results are obtained when the calcium citrate or juice contains other acids which yield sparingly soluble calcium salts. The presence of oxalic acid or of tartaric acid may be detected by the fact that the cold, neutralized solution gives a precipitate in the cold with calcium chloride.

The above-described methods are those which are generally adopted in the citric acid industry. The following methods, selected from the numerous processes which have been suggested may be here briefly summarized.

Ulpiani and Parozzana have described a method of analysis which, according to Klapproth gives satisfactory results for citric acid even in presence of other organic acids. This method depends upon the fact that citric acid, in presence of a sufficient quantity of calcium chloride, is precipitated by sodium hydroxide *in the cold,* when the whole of the acid is saturated, and the *hot solution* when one-third of the acid is saturated.

Spica has described a method based on the formation of carbon monoxide when citric acid is gently warmed with concentrated sulphuric acid; one molecule of carbon monoxide is obtained for each molecule of citric



(Allen: Commercial Organic Analysis)

FIG. 16.—Apparatus for the determination of citric acid.

acid present. The citric acid is first precipitated as calcium citrate (as in Warington's method) and the citrate then decomposed by the sulphuric acid in the apparatus described below (Fig. 16):

The upper part *A*, is fitted to the flask, *B*, (150-c.c. capacity), by a ground joint, and the tubes, *D* and *E* and *C* and *E*, may be connected respectively through the tap, *R*, as also may the flask and the exterior. Two gm. of the calcium citrate, moistened with water, are introduced into *B*, and the air in the flask is completely displaced by carbon dioxide, the absence of air being ascertained by means of an auxiliary nitrometer, filled with potassium hydroxide solution (1 : 5) and attached to the T-piece. Twenty-five c.c. of concentrated sulphuric acid are then run into *B* from *A* and a slow current of carbon dioxide occasionally shaken, the carbon monoxide evolved being collected in a nitrometer of 200-c.c. capacity, of which the lower part *B'* (100-c.c. capacity) is graduated in fifths of a c.c. When the volume of gas becomes constant, the nitrometer is allowed to stand for half an hour and then after washing the gas with potassium hydroxide solution, introduced through *I*, the volume is read and the usual corrections are made for temperature and pressure. One c.c. of carbon monoxide at 0°C. and 760

mm. indicates 0.009407 gm. of citric acid ($C_6H_8O_7$, H_2O). The same apparatus may be used for the determination of carbonate in a citrate, by decomposing with a known volume of concentrated hydrochloric acid and measuring the evolved carbon dioxide over water.

The foregoing process is obviously useless when other organic acids are present which evolve carbon monoxide.

Estimation of citric acid in presence of other acids.—Beau's modification of the method of Denigès is shown by Gowing-Scopes to give unreliable results owing to the action of the hydrogen peroxide (added to remove the manganese dioxide) upon the precipitated mercury dicarboxysulphoacetone. Other reagents tried for removing the manganese dioxide either oxidized or reduced the precipitate, which in hot solutions was also oxidized by manganese dioxide. A compound containing 72.5 to 74.0 per cent of mercury and apparently similar to, if not identical with, the compound of Denigès' was obtained by the use of a reagent prepared by adding 68 c.c. of strong nitric acid to 51 gm. of mercuric nitrate and 51 gm. of manganese nitrate, diluting the mixture with 100 c.c. of water, and finally, making up the solution to 250 c.c. and filtering. For the determination of citric acid a quantity of the substance containing not more than 0.04 gm. nor less than 0.001 gm. of the acid is exactly neutralized with N/10 alkali, using phenolphthalein as indicator, and, after the addition of 10 c.c. of the reagent, the liquid is diluted to 200 c.c., and boiled for three hours beneath a reflux condenser. The precipitate is washed by decantation, collected on a weighed Gooch crucible, and again washed in the crucible, which is then dried in a water-oven until nearly constant in weight (about five hours). The residue should then be of a cream color, any yellow coloration indicating the formation of basic salts, which will cause the results to be too high. One-sixth of the weight of the precipitate gives the amount of citric acid. In sixteen test estimations with pure citric acid within the limits stated above, the maximum error was +0.0004 gm. Good results were also obtained in the presence of tartaric, succinic, oxalic, benzoic, and phosphoric acids, but when malic, lactic, or salicylic acids were present the results were too high. Salicylic acid gives, with the reagent, a salmon-colored precipitate, probably a nitro-derivative, while gallotannic acid gives an orange-brown precipitate. The precipitate given by citric acid decomposes suddenly when heated. It is very soluble in hydrochloric acid, in strong sulphuric or nitric acid, and in solutions of halogen salts.

In the absence of sugars it is not necessary to precipitate the citric acid as barium citrate and redissolve with phosphoric acid. An accuracy of 2 per cent to 4 per cent is claimed.

The foregoing process does not give satisfactory results in the presence of malic and tartaric acid and is therefore not applicable to the examination of fruit juices. In such cases, according to D. S. Pratt the following method is of especial value.

Fifty gm. of fruit juice are treated with 110 c.c. of 95 per cent alcohol to remove pectin bodies. After fifteen minutes the solution is filtered and the residue washed with 95 per cent alcohol. The resulting solution is diluted with water to an alcoholic strength of about 50 per cent and a 20 per cent aqueous solution of barium acetate is added to precipitate the

citric acid. After stirring, allowing the precipitate to settle, and filtering the solution, the precipitate on the paper is washed with 50 per cent alcohol to remove sugars and then the paper and its contents are dried to remove the alcohol. The residue is then warmed with 50 c.c. of water and 3–5 c.c. of syrupy phosphoric acid to dissolve the barium citrate. This mixture is filtered into a graduated flask and the paper washed until the filtrate measures 100 c.c. An aliquot part of this solution containing 0.05–0.15 gm. citric acid is measured into a 500-c.c. distilling flask, 5–10 c.c. phosphoric acid are added with 400 c.c. hot water, and the flask is heated. When briskly boiling 0.05 per cent potassium permanganate solution is run in by means of a dropping funnel at the rate of one to two drops per second until the pink coloration is permanent.

The acetone formed by the oxidation distils off as fast as it is formed into 30–40 c.c. of Denigès reagent. The distillation is continued till only 50–100 c.c. of solution remain in the flask.

The mixture in the receiver is then boiled gently under a reflux condenser for forty-five minutes after the liquid becomes cloudy. It is then filtered hot through a Gooch crucible, washed with water, alcohol, and ether, and dried in a water oven for thirty minutes. The weight of precipitate multiplied by 0.22 gives the weight of citric acid originally present.

Fresenius and Grunhut claim that the methods based on the precipitation of acetone dicarboxylic acid as given above are untrustworthy in the qualitative detection of citric acid in wines. For this purpose they recommend Krug's modification of Moslinger's test which is carried out as follows:

Fifty c.c. of wine are evaporated to a syrup. The syrup is treated with 95 per cent alcohol and filtered to remove tartrate and then evaporated to remove alcohol. Ten c.c. of the resulting liquid are treated with acetic acid and lead acetate. In the presence of citric acid a precipitate will be obtained which dissolves on heating and reappears on cooling.

Tests of purity of citric acid.—Lead, arsenic, and ash are treated for as under tartaric acid, the limiting quantities allowed being the same as in the case of tartaric acid. It is usual, however, in commerce to require a higher degree of freedom from lead than in the case of tartaric acid; the amount present seldom exceeds ten parts per million. Arsenic is generally entirely absent.

The following are the requirements of the *British Pharmacopoeia, 1914:* 1 gm. dissolved in water requires for neutralization 14.2 c.c. of N/1 solution of sodium hydroxide; yields no characteristic reaction for copper or iron and not more than a very slight reaction for calcium or sulphates. *Lead limit* 20 parts per million. *Arsenic limit* 1.4 parts per million. One gm. of powdered citric acid mixed with 10 c.c. of sulphuric acid in a test tube previously rinsed with sulphuric acid acquires not more than a pale-yellow color when kept at a temperature of 90° for one hour (absence of tartaric acid); ash not more than 0.05 per cent.

The following color tests, based on Pusch's method of detecting tartaric acid in citric acid are described by Hill. 0.5 gm. of the sample and of pure citric acid are placed in separate test tubes (6 in. × ⅝ in.)

and 5 c.c. of sulphuric acid added to each. The tubes are placed simultaneously in an ordinary Bunsen flame; at the end of thirty seconds they are withdrawn and examined. The results obtained with acids of different degrees of purity are as follows:

Pure Acid	Lemon-yellow Solution
5.0 per cent tartaric acid	black, sulphur dioxide abundant
1.0 per cent tartaric acid	deep brown-black, sulphur dioxide evident
0.5 per cent tartaric acid	deep red-brown
0.25 per cent tartaric acid	red-brown
0.1 per cent tartaric acid	reddish brown
0.01 per cent tartaric acid	brownish yellow

With careful manipulation and sixty seconds heating, 0.0001 per cent of tartaric acid is said to be easily detected; even 0.00001 per cent gave a distinctly deeper tint, in good light, than the control tube. The test is also applicable to citrates, 1 per cent of tartrate being easily detected. The foregoing method is also applicable to detect sugar in citric acid; the reactions obtained are:

1 per cent of sugar	cherry-red, sulphur dioxide distinct
0.1 per cent of sugar	sherry color, sulphur dioxide evident
0.01 per cent of sugar	yellowish red, sulphur dioxide perceptible
0.001 per cent of sugar	reddish yellow
0.0001 per cent of sugar	reddish yellow

It was also found that 0.5 per cent of sugar could be detected, in tartaric acid, by the coloration after an hour's contact with cold sulphuric acid; by heating for ten seconds in the flame the control tube remained practically unaffected, with 1 per cent of sugar a red solution was obtained, and with 0.5 per cent a red-brown ring.

Haussler describes a characteristic color reaction given by citric acid with vanillin; the solution is evaporated to dryness after adding an alcoholic solution of vanillin and the residue treated with three drops of dilute sulphuric acid, heated on a water bath for fifteen minutes dissolved in water and ammonia added. A bright-red coloration is obtained with 0.002 gm. of citric acid. The red coloration is not given by tartaric, malic, oxalic, malonic, benzoic, salicylic, acetic, lactic, or succinic acids.

BITTER GLUCOSIDES

HESPERIDIN AND HESPERITIN

Hesperidin is a glucoside freely distributed in the family *Rutaceae*. It has been shown to be present in the ripe and unripe fruit pulp of *C. aurantium, C. limonum, C. limetta, C. sinensis, C. nobilis,* in the leaves and twigs of *C. aurantium,* different species of *Diosma, Barosma,* and other plants. On the other hand it is absent in *C. decumana.*

Hesperidin was discovered by Lebreton in 1828, but was more fully studied by Hoffmann, 1876.[1]

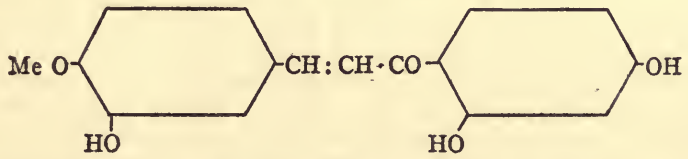
[1] *Berichte der deutschen chemischen Gesellschaft,* 9, 26, 685; *ibid.* (1876), pp. 250–52.

Method of preparation.—Cut and bruised oranges are covered with dilute alcohol, with potassium hydroxide added in excess to neutrality. The liquor is filtered after two days, when impure hesperidin is precipitated by hydrochloric acid. The precipitate is boiled with acetic acid for ten minutes, after cooling filtered from the resinous mass that is left; on standing the hesperidin gradually separates from filtrate in white fine needles. From 4,000 oranges about 6 oz. of hesperidin is obtained.

Properties.—Its formula is $C_{22}H_{26}O_{12}$ and it is a glucoside, as is shown by the reaction with dilute sulphuric acid, whereby it is decomposed into hesperitin, $C_{16}H_{14}O_6$, glucose, $C_6H_{12}O_6$, and rhamnose.

The white, odorless needles, are almost insoluble in cold water, difficultly soluble in hot water, more soluble in alcohol and hot acetic acid, insoluble in benzol, chloroform, and ether. Ammonia, dilute alkalies, alkaline earths, and pyridine dissolve hesperidin easily, the solution being yellow to orange. If hesperidin is evaporated with dilute KOH and the residue heated with dilute H_2SO_4 a red to violet color is obtained. By heating with dilute H_2SO_4 hesperidin splits into rhamnose, glucose, and hesperitin. It does not reduce Fehling's solution. Hesperidin is always dissolved in the cell sap and separates out on the removal of water. The addition of glycerine causes crystals to form. The melting-point of hesperidin crystals is 270° according to Borodin. It is not appreciably fermented by yeast.

Tutin has given the following formula to hesperitin which has been confirmed by the work of Oesterle and Kueny:



Microchemistry.—It is present in living cells in dissolved form. If ripe or unripe oranges are placed in absolute alcohol hesperidin crystallizes out in the form of sphaerocrystals. The same result may be obtained by placing the pieces of fruit in glycerine, though in this case the sphaerocrystals are less beautiful. Also by drying the tissue of the orange, hesperidin crystallizes out in the form of needles or incomplete sphaerites. The crystallization of the glucoside out of alcohol takes place slowly; one must wait a long time. If it is desired to produce this result quickly the following method may be used. Cut an orange in two crosswise and simply lay down the two halves with the cut surface upward. After one-quarter to one-half hour the hesperidin forms on the cut sections of the peel in the form of needles and sphaerocrystals. One might think that the same results could be obtained by pressing out a drop and allowing it to evaporate. Such is not the case. Hesperidin crystals from the tissue show the same solubility relations as pure hesperidin; e.g., their solubility in aqueous and alcoholic alkalies with yellow color, their difficult solubility in water by virtue of which they may be distinguished from inulin sphaerites to which they are similar in appearance. Hesperidin crystals are

doubly refracting, and the sphaerites behave in polarized light like those of inulin. According to Pfeffer hesperidin appears not only in the fruit but also in all pith, bark, leaf, and flowers of the orange. It is especially plentiful in the fruit nodes and bloom buds and in the unripe fruits. It is found in the fruit in all the parenchymatic cells of the fruit flesh and pulp. In order to exclude disturbing substances (alkaloids) treat the preparation with tartaric acid alcohol and then with hot water. Put a large number of sections on a slide in a few drops of KOH, remove the sections after some time, let the solution dry up, and add the H_2SO_4.

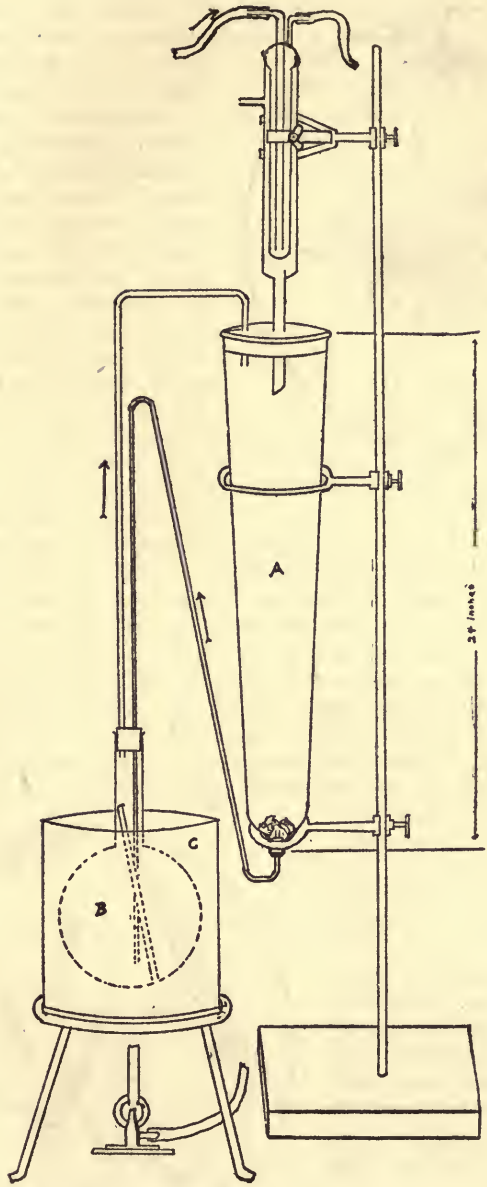
ISOHESPERIDIN AND AURANTIAMARIN

Tanret found in the rind of the bitter orange (*C. aurantium* L.) (1) a crystalline acid, $C_{44}H_{28}O_{14}$; (2) a non-crystalline resinous body; (3) hesperidin; (4) isohesperidin, a crystalline glucoside isomeric with hesperidin; (5) aurantiamarin, another glucoside to which, in part, the bitterness of the peel is due.

NARINGIN

The bitter principle from the chopped, fresh peel of the grapefruit is called naringin. A method for its extraction was devised by Zoller. An extraction apparatus according to Figure 17 was set up. The percolator *A* held the finely chopped peel from fifteen large grapefruit. A small tuft of glass wool was placed in the bottom of the percolator to prevent the return tube from being stopped up. One and one-half liters of 96 per cent alcohol were placed in *B*. *C* contained water for the bath. The operation is automatic and simple after the first dumping of *A*. Ten hours are sufficient for the complete extraction of the glucoside from each charge of peel. Of course, the oils, resins, and other substances are extracted along with the glucoside, but no pectose material is present in the extract. To facilitate the evolution of a continuous current of alcohol vapor from *B*, a glass tube of 0.5 to 1.0 cm. bore is sealed at one end and inverted in the round bottom flask. The vapor expanding in this tube causes a continuous succession of bubbles, which tend to prevent both bumping and froth. The extract from *B* is then poured into flask *D* of Figure 9 on page 47. *E* is again used for a water bath, the temperature of which must not remain above 80°. *D* is connected with a Hopkins condenser with a glass seal, and the condenser in turn connected with a receiver to which suction to the pressure of 10 mm. may be applied. A fine capillary tube with stopcock extends to the bottom of *D* to regulate the distillation by means of a free current of air. The alcohol and oils are collected in *F* and may be used for the extraction of another charge of peel without distilling.

The residue in *D* should be a golden-yellow syrup, which is taken up in water and treated with a few cubic centimeters of 25 per cent basic lead acetate solution to precipitate out the material other than naringin, the glucoside. The mass is filtered without suction and the excess lead removed with hydrogen sulphide, from hot solution. The clear filtrate from the PbS precipitate is allowed to stand for a few hours, when the white rosettes begin to form on the sides of the containing vessel, analogous to those from the fermenting liquor. Mild shaking induces an instantaneous



(Zoller: Jour. Ind. and Eng. Chem.)

FIG. 17.—Apparatus for naringin extraction

FIG. 18.—Naringin. Glucose and rhamnose ester of naringenin.

crystallization filling the container. Considerable heat is evolved. Purification is accomplished as previously mentioned.

The white crystals are monoclinic, glistening, and when compressed are light cream in color. They are exceedingly fluffy so that the quantitative yield appears larger than it really is—from 0.2 gm. to 1.6 gm. per fruit. The crystals are soluble in water at 20° to the extent of one part in 8,000 of water, though even at this dilution it is intensely bitter. This emphasizes the fact that it is of a greater degree of bitterness than quinine, for which it has often been mistaken.

After the determination of its physical constants, elementary analysis, and chemical reactions together with the physical and chemical properties of its hydrolytic products, Zoller was certain that he was working with the same compound that DeVry discovered in 1857, in the flowers of the grapefruit trees in Java. DeVry states that it occurs in all parts of the *Citrus decumana* though to a much greater extent in the freshly opened flowers. While both he and Hoffmann, and later Will, conducted researches on this glucoside, they state that they obtained their raw product from the residue remaining in the distillation pots at Java after removing the "neroli oil" from the flowers of the grapefruit tree by steam distillation. Both DeVry and Hoffman were unable to find this same bitter substance in the flowers or fruit of any of a host of other citrus fruits, including the bitter orange.

Hoffman applied the name "naringin" to the glucoside which DeVry and he investigated. Will retained the same term in his investigations with Tiemann. The term originated, according to Hoffman, from the Sanskrit word "naringi" for orange.

Solutions of naringin in ethyl alcohol and water are laevo-rotatory; the molecular rotation in alcohol at 18°C. is —65.2. Its empirical formula

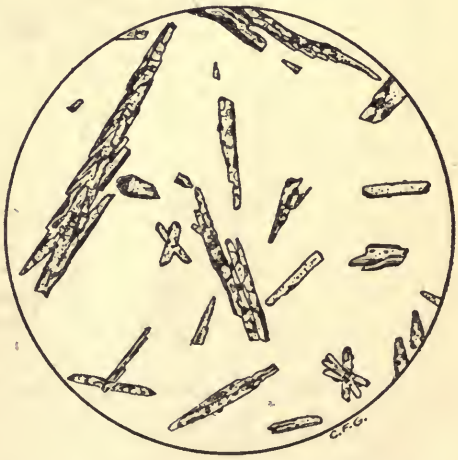


FIG. 19.—Naringenin. Phloroglucinol ester of parahydroxy cinnamic acid.

as determined from carbon and hydrogen combustion, as well as from a study of its cleavage products, appears to be $C_{21}H_{26}O_{11}\cdot 4H_2O$ (air-dried). Over sulphuric acid it loses three molecules of water, and when dried at 120°C. it loses the remaining molecule of water. In the latter state it is in the form of an impalpable powder, colored a faint tinge of yellow. When naringin is hydrolyzed with dilute (5 per cent) HCl or H_2SO_4, it forms a mixture of rhamnose and glucose, though the quantity of glucose is much smaller than that of rhamnose. At the same time a highly crystalline solid separates, insoluble in water, and was found to be the phloroglucinol ester of *p*-hydroxy-cinnamic acid.

Zoller calls attention to the behavior of the glucoside which governed the choice of the extraction method above for its isolation from the peel. When the air-dry naringin is heated in a receptacle over a free flame it melts at about 83°C., and forms a syrupy mass which turns brown on gently increasing the temperature to 100°C., above which violent evolution of H_2O vapor takes place and a hard, glassy, dark-brown mass results. This mass is still bitter but dissolves with difficulty in water. On the other hand, when a water solution of the naringin (pure crystals) is boiled, it rapidly turned yellow to brown, the bitterness gradually disappeared and when evaporated on a steam bath a resinous mass resulted, possessing the odoriferous principles of caramelized sugars together with those of cumarin and certain phenols. No naringin could be extracted from the mass. Likewise, when the peel was ground, dried at 110°C., and lixiviated with water, very little naringin was obtained. Hence in the separation of the glucoside from the fresh fruit, temperatures above 80°C. should be avoided. In the steam distillation of the peels some of the naringin is hydrolyzed by the steam, though the temperature in the distilling flask seldom registered above 85°C.; stronger suction would prevent this decomposition.

The quantity of glucoside in the grapefruit examined was approximately as given in Table XXIII.

TABLE XXIII

Variety of Fruit	Age of Fruit	Weight of Fruit (Grams)	Quantity of Naringin from Peel only (Grams)
Indian River	Fresh market	770	0.62
	Old* market	715	0.35
Walters	Fresh fruit	682	0.50
	4 mos. at 15° C.†	695	0.24
Marsh, seedless	Fresh market	539	0.36
	Old market	570	0.08

*"Old" signifies that the fruit was of the same variety as the fresh market, but that it had been kept for some time between analyses, in order to determine the effect of deterioration on the bitterness. The "Walters" was secured directly from a fruit exchange and some of the fruit kept at constant temperature for the time specified.

†It is difficult to give the age to any great degree of exactness.

From Table XXIII it is quite evident that there is a diminution in the naringin content during storage, more noticeable in some varieties than in others. What has happened to the glucoside is revealed when the sugar content of the pulp is examined over a like period. Of course, it is not argued in Zoller's article that the increase in sugar content of the pulp during storage is traceable solely to the glucoside, in the face of the large pectose content. But a portion of it, he considers, may be derived from the hydrolyzed glucoside by the aid of the enzymes present in the fruit. Certain flavors and "pink spots" which develop simultaneously with the decrease in naringin and increase in sugars may be traceable to the glucoside, when the reactions of this substance are better understood.

FODDER

According to Cheney the lemon pulp from which the juice has been pressed is used in Sicily for either fertilizer or fodder. In southern California this practice has not yet come into use. Many refuse nitrogenous substances are now being utilized in the United States for cattle food, substances which of themselves are unpalatable. These when mixed with black strap or refuse from sugar refineries are converted into edible food material.

PAPER

Among the uses which have been suggested for the refuse orange and lemon pulp is that for paper. So far as known, however, no experiments have been conducted along this line.

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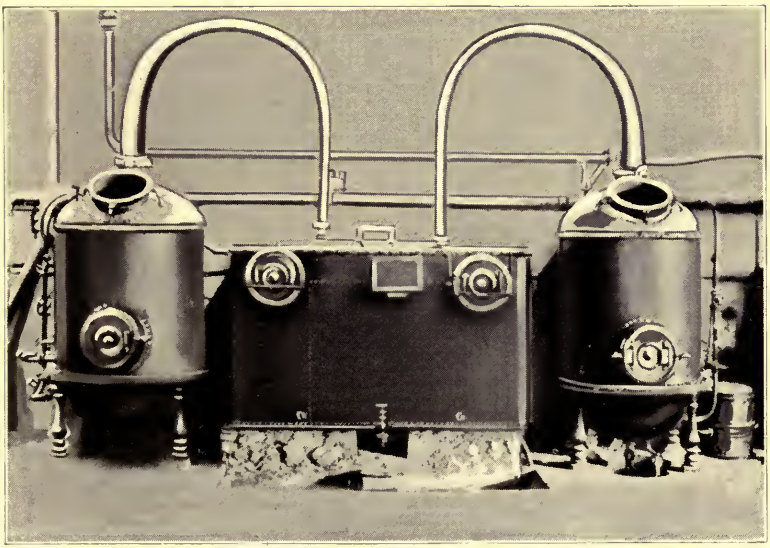

(La Parfumerie Moderne)

DISTILLATION OF NEROLI AND PETITGRAIN OILS.

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CHAPTER VI

PRODUCTS FROM THE SEEDS

The "pastazzo" or residue from washing citrate of lime, etc., in the manufacture of citric acid contains a large quantity of seeds. Bertolo considers that this waste product, of no commercial value, could be profitably utilized for oil extracted by pressure or with solvents. Little oil is obtained from the seeds by pressure, but extraction with carbon disulphide, petroleum ether, or benzene gives 30–35 per cent oil according to the degree of maturity. The oil from the press is light yellow and rather fluid, with the odor of lemon and with a somewhat bitter taste. That extracted with solvents is somewhat turbid and gradually deposits a considerable quantity of pasty sediment consisting chiefly of solid saponifiable matter. The dark-yellow color of

TABLE XXIV

	Sinensis	Fortunella	Junos
	Seed		
Water	44.67	39.06	10.60
Crude fat and oil	19.52	25.50	21.88
Nitrogen	1.71	1.38	2.39
Crude protein	10.68	8.66	14.94
Non-nitrogenous substances	18.70	17.25	44.63
Fiber	4.68	7.23	5.41
Ash	1.75	2.30	2.53
	Oil		
Color	Pale golden yellow	Brown-yellowish green	Golden yellow
Nature	Semi-drying	Semi-drying	Semi-drying
$d_{15°}$	0.9200	0.9223	0.9221
$n_{D20°}$	1.422	1.4730	1.4720
Acidvalue	0.90	1.05	4.97
Saponification value	192.7	193.4	195.1
Iodine value (Wijs)	105.27	113.03	100.42
Unsaponified matter	1.22	1.22	1.28
Fatty acids solid	27.1	19.1	22.2
Fatty acids liquid	66.2	74.7	71.3
Melting-point of fatty acids	58–58.5°	52–52.5°	52–53°
Iodine value solid	5.82	34.23	43.71
Iodine value liquid	142.85	137.29	130.54
Neutralization value solid	213.5	205.8	199.2
Neutralization value liquid	193.3	193.6	196.8

the oil and its green fluorescence are not removed by repeated washing with hot water or dilute sulphuric acid. The oil is semi-drying and resembles cottonseed oil, containing a very high percentage of liquid glycerides and less than 28 per cent solids.

Diedrichs in investigating orange and lemon seeds found oils in them which had the following chemical and physical properties: Lemon seed oil, yield 50 per cent, iodine No. 107.26, saponification No. 195.98. Orange seed oil, yield 57 per cent, iodine No. 97.26, and saponification No. 196.37.

S. Kobayashi investigated the following orange seeds and orange seed oils. The air-dried seeds from *Sinensis* Engl. (yield 2 per cent), of *Fortunella Japonica* Swingle (3.7 per cent), and of *Junos* Mak. (9.50 per cent) were crushed into small pieces and the oils extracted with petroleum ether. The oils were purified by steam distillation, and in the latter two cases the oils were treated with Kambara-clay (10 per cent) for decoloration.

Hewer analyzed oils from orange seeds which seeds were separated by centrifuge from orange pulp used in marmalade. The inodorous oil was extracted by petroleum ether with a yield of 37.5 per cent. This was easily saponified and had a saponification No. 193.7, iodine No. 100.3, and specific gravity at 15°C. of 0.9208.

Fisch and Gattefosse (1920) analyzed the seed oil from *"Citrus aurantium* s. sp. *Lima* var. *fusca."* They secured the following values: specific gravity 0.930, melting-point —2.05, solidifying-point —3, viscosity (Engler) at 25° 5.7, flash point 210°, combustible point 210°, saponification No. 177.3 (easily saponified), iodine No. 83.8, total volatile acidity 94 per cent, combined volatile acidity 91.1 per cent, free volatile acidity 2.1 per cent, melting-point volatile acidity 28°, solidifying-point volatile acidity 27.40°.

Fisch and Gattefosse (1921) also worked with citron seed oil (*"Citrus medica* var. *acida"*) which they obtained from French equatorial Africa. The expressed oil is an amber viscous liquid with an agreeable odor and fluorescence analogous to certain mineral oils. It has the following physical and chemical constants: melting-point 2.05°, solidifying-point 3.00°, specific gravity 0.930, optical rotation 0.0, refractive index at 15° 1.4757, viscosity (Engler) at 25° 5.7, point of inflammability 210.00°, point of combustion 247.00°, total volatile acidity 94 per cent, combined volatile acidity 91.1 per cent, free volatile acidity 2.9 per cent, melting-point volatile acidity 28.00°, solidifying-point volatile acidity 27.40°, iodine No. 83.8, saponification No. 177.3.

It is thought that this oil may be used in soap-making and in the replacement of raisin-seed oil in rubber-making.

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CHAPTER VII

PRODUCTS IN WHICH THE ENTIRE FRUIT IS USED[1]

MARMALADE

Orange marmalade, most familiar to us in the form of the "Dundee marmalade," consists essentially of a cooked mass of sugar and fruit. Dundee marmalade is made in Scotland of bitter Seville oranges. The oranges are imported from Southern Europe, and, after necessary cleaning, the pulp and the peel are separated and the seeds extracted by special highly developed machinery, patented in England. The white pith adhering to the peel and containing bitter substances, is separated from the peel, and the peel is then placed in large vats and subjected to steaming for a number of hours in order to soften materially and possibly drive off a portion of the essential oil so that the sugar in the after-process of cooking may more readily penetrate and produce a transparent finished product. The softened peel is then run through a peel-shredding machine, which automatically cuts the peel into very fine shreds. The pulp meanwhile has been subjected to a thorough grinding process to produce as fine a division of particles as is reasonable and practicable. This pulp is then mixed with a proper proportion of shredded peel and placed in kettles for cooking. Some factories add sugar directly to this prepared mass, while others give a preliminary boiling before the sugar is added with water, in order to permit the sugar more completely to penetrate the peel and the fibrous bodies contained in the pulp. When the mass of orange peel has been subjected to boiling for some time with sugar, and the proper consistency is reached, it is placed in jars and sealed.

The characteristic of the Dundee marmalade is its slight bitterness and its tart flavor; sugar being the cheapest ingredient in it, formerly approximately 2 cents per pound compared to American sugar at 4 and

[1]United States patents involving the use of whole fruit are: H. A. Hughes, No. 534368, February 19, 1895 (preserved in sugar); A. P. Gaines, No. 683112, September 24, 1901 (dehydration of fruit in hot sugar); F. M. Libby, No. 737119, August 25, 1903 (fruit compound with limes, pickled); A. T. Jones, No. 827730, August 7, 1906 (dry fruit in hot vacuo); O. Paucksch, No. 92421, June 8, 1909 (desiccating apparatus); G. D. Harris and J. S. Pollard, No. 1017411, February 13, 1912 (pieced and dried, hot air); E. W. Cooke, No. 1025374, May 7, 1912 (dehydration by air); C. N. Tinkelpaugh, No. 1033637, July 23, 1912 (desiccation with sun and sugar); H. H. Harrison, No. 1062969, March 27, 1913 (dried fruit).

5, the product is loaded with sugar in order to reduce the cost of manufacture to as low a point as possible.

In California the bitter Seville orange is not available. Here marmalade is manufactured on a large scale not only with different fruit but by very different methods.

The fruit is cleaned if required, and then sliced with what is known as a "kraut cutter," which is simply a revolving disk upon which is screwed semi-circular knives which cut the fruit into slices. These slices are sometimes subjected to a preliminary soaking in water, but more often are placed immediately in kettles with sugar and water, brought to a boil, and boiled until a proper consistency is reached. As the fruit is the cheapest ingredient entering into this product, the marmalade is loaded with fruit, although large consumers of this product in bulk usually specify 50 per cent sugar and 50 per cent fruit in the finished product.

The orange marmalade so made is a rather sweet mass not having many characteristics of the Dundee marmalade. It has, however, certain uses, as in the manufacture of biscuits and the like.[1]

To produce from the sweet orange a marmalade very similar to Dundee marmalade the fruit is treated as described under this but with the addition of some more acid fruit, such as the grapefruit or lemon.

One of the characteristics in which the usual orange marmalade produced in America differs from the Dundee product is the fact that it jells very readily. It is a solid mass, rather than a syrupy mixture. This is due to the fact that the white pith of the rind bearing the pectin is not removed.

The combination of various fruits have also been made into marmalade, which have their own peculiar pleasant characteristics. The grapefruit has been made into marmalade quite extensively and has found favor as a competitor with the Dundee product because of its inherent tartness and slight bitterness.

One California plant makes orange marmalade according to the following process. The fruit is first sorted, then goes to an automatic slicing machine so that all of the valuable properties of the fruit may be easily got into suspension in the first cooking process.

From the slicing machine the material is dropped into large steam-jacketed kettles, where sufficient water is added to keep the fruit from burning, and the entire mass is boiled into a heavy pulp. After a given time, this pulp is run through a continuous press, where the acid, fruit sugar, and other valuable properties of the fruit are pressed out and col-

[1]One American concern has used many cars of this orange marmalade in making a product similar to what is known as "Fig Newtons."

lected in a large tank, in which the temperature is kept uniform and the juice standardized for all of its valuable properties.

From this tank the juice is pumped through a large filter, which has a capacity of over 200 gal. an hour, and in this filter all of the flocculent matter that is carried through the press by the juice is removed, and the resultant product is the essence of the fruit—clear, sparkling, of uniform composition, and without any of the fibrous substances of little or no food value, so abundant in orange products.

From the filter the juice is carried by glass-lined pipes to the cooking department where it is mixed with a uniform quantity of sugar and the individual lots cooked to a uniform consistency by expert women cooks. A small part of the very best fruit is selected, choice strips of peel are taken off from the center of these and run through a special device known as a "shredding machine," which chops the strips of peel into very fine shreds. This raw shred is then put in a steam cooker and cooked until it becomes very soft. The water is then pressed off and the dry cooked shred is added to the marmalade before it reaches the finished point. This shred adds the flavor of the peel as well as gives a delicate body to the finished marmalade.

After the pans of marmalade have reached the finishing point, they are immediately removed from the cooking-table. The marmalade is emptied into a large enameled tank, which supplies the filling machine. On one side of the filling machine is the glass-washing machine, where the empty glass is carried through a bath of hot water and live steam. From the washing machine the dry sterile glasses are delivered to the filling machine.

After leaving the filling machine the glass is passed over an inspection table, where each glass is candled by a woman inspector. At this point, any jars containing thick or scorched shred or other discolorations are removed. The inspector places the metal cap on the glasses that pass inspection. The glass and cap are taken off the belt by a capping-machine operator and the caps are automatically sealed down after exhausting in a 25-inch vacuum.

At Anaheim, California, a company was organized in 1921 with a capitalization of $100,000. This company concentrated marmalade, making it into cubes, 1 cu. in. in size. A cube placed in boiling water for ten minutes forms marmalade. A small amount of sugar and a bit of orange peel may be added. The entire process of manufacture requires one day and one ton of fruit will make 4,000 cubes.

CULL CITRUS FRUITS AS A FERTILIZER

Waste citrus fruits are of value as an orchard fertilizer. As such they add humus to the soil, a constituent in which citrus soils generally have only a small amount. They also by their decomposition return to the soil many of their inorganic constituents in very nearly the proportion that is required. The organic contents are mostly lost during the decay of the fruit. Several undesirable factors, however, are met with in this practice such as the putrid smell of the decaying organic matter and the danger of infecting the fruit on the trees with brown rot and other fungi. These undesirable factors are sometimes eliminated (at the sacrifice of humus value) by burning the fruit and using the ashes as fertilizer, or the fruit may safely be thoroughly plowed under.

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CHAPTER VIII

PRODUCTS FROM THE FLOWERS[1]

Oil of orange flowers was known as early as the sixteenth century. Its distillation was described for the first time by Porta. About a century later, in the year 1680, it appears to have become a fashionable perfume through the Duchess Flavio Orsini, Princess of Neroli, hence the name *essence of neroli.* On account of its delicate pleasant odor, the oil has been able to hold its reputation as one of the finest of flower perfumes. This is also true of the distilled orange-flower water, or *Aqua naphae,* which is used extensively to impart an aroma to food, confections, beverages, and toilet articles. The distillation of orange flower oil was described by Benatius in 1806. The oil was investigated in 1825 by Bonastre and in 1828 by Boullay.

True neroli oil is produced from the flowers of the bitter orange, *Citrus aurantium.* Other trees of citrus also produce delicately scented flowers, but their fragrance is inferior to that of the bitter orange.

The center for the neroli oil industry is in the southern part of France where the bitter orange is cultivated for this purpose only. The following localities are noteworthy because of their large groves: Cannes, Le Cannet, Vallauris, and Golfe Jouan; also the following localities near to the base of the Maritime Alps, viz., Biot, Cagnes, La Colle, La Gaude, Gattières, St. Jeannet, Vence, Tourettes, Gorges du Loup, and Le Bar.

The principal harvest of blossom lasts from the beginning of May to the middle of June and, in good years, amounts to from 2.5 to 3 million kg. Much smaller is the harvest of fall blossoms.[2] In 1909 it amounted to 270,000 kg. The flowers are collected by women with the aid of ladders. Each blossom has to be pinched off with the finger nails and is dropped on cloths spread underneath the tree. Only the fully expanded flowers are picked and all injury to the buds must be

[1]Orange flower oil is used in perfume and as a flavoring agent in syrups. Its odor is due principally to methylanthranilate. This substance is made synthetically from coal tar, and in 1920 was produced by six United States firms. A synthetic product sold under the name of neroli is used largely as a perfume by soap makers. Comparative prices of genuine and synthetic oil of neroli are tabulated in Part II of this book.

[2]Details as to yields see *Report of Schimmel & Co.* (October, 1899), p. 38; (October, 1902), p. 52; (October, 1903), p. 49. Also P. Jeancard and C. Satie, *Bulletin de la Société de Chimie,* Vol. XXIII, Series 3 (1900), p. 605; Vol. XXIX (1909), p. 992.

carefully avoided. In order to obtain satisfactory prices for the flowers, the owners of the groves have not long ago combined in a syndicate (Société coopérative de production des propriétaires d'oranges des Alpes-Maritime), to utilize the flowers not sold to others. The price of the blossoms fluctuates between 0.5 to 1.35 fr. per kilogram.

The essential oil obtained by distillation is called "neroli"; that by maceration or absorption in fats and volatile solvents is called true "orange flower oil." There is a marked difference in the products obtained in these various ways; this is especially true of the oil obtained by distillation. The oil thus produced, although suprisingly delightful, has quite a different odor from the fresh orange flowers. Of the other methods, the ones by solvents and by absorption (*enfleurage*) yield the finest article true in odor to the natural flower.

The method most generally followed is distillation. Among the reasons for this preference is the higher yield of oil obtained. From 1,000 kg. of flowers the following are the results:

	Gm. of Oil
1. By distillation	1,000
2. By maceration	400
3. By absorption (i.e., *enfleurage*)	100
4. By volatile solvents	600

Another advantage of the distillation method consists in the simultaneous production of a quantity of orange flower water. In former times when the perfumery industry was still in its infancy, the orange flower water was the main item of production, the oil itself being considered a by-product and sold cheaply. Now conditions are reversed.

The yield of oil is greatly influenced by the temperature and atmospheric conditions prevailing at the harvest time. In warm and dry weather it may run up as high as 1,400 gm. per 1,000 kg. of flowers; under exceptionally favorable conditions, it may even reach 1,700 gm. per 1,000 kg. But under adverse conditions such as damp, cool, and variable weather, a considerable dimunition is experienced. As a rule, toward the end of the flowering season, on account of the warmer temperature, the larger yields are obtained. The flowers are distilled immediately after gathering. Special distilling apparatus is employed whereby the distillation is effected very rapidly and completely, and in a few weeks enormous quantities of flowers are worked over.

In connection with orange flower oil it is interesting to note that the oil from spring flowers is similar to the oil from the young branches whereas oil from fall flowers is similar to oil from the older branches. Chemically the oil from the spring flowers is poorer in esters and total

alcohols. From such a consideration Laloue concludes terpenes to be formed in the green parts of plants.

The importation of neroli into the United States has greatly increased during the last sixteen years as is shown in the table in the Appendix in Part II of this book. The value per pound, however, has decreased. This particular branch of the citrus product industry has no direct bearing on American citrus production as neroli is not made here. Nevertheless it has an indirect influence on the other phases of the situation as can be easily comprehended. Orange flower oil might prove a worthy field for investigation.

OIL OF NEROLI BIGARADE

Oil of neroli from the flowers of the bitter orange is more valuable and is known as "Oil of Neroli Bigarade" (ordinary neroli oil; the oil from the sweet orange flower is known as "Oil of Neroli Portugal"). The greater part of the oil of commerce is distilled in Southern France, one of the chief centers being Vallauris. In this region the yield of oil varies greatly according to the time of season when the flowers are collected. The season commences about the last week in April and ends about the last week in May. The early flowers give ½ gm. of oil per kilo, the late flowers double this amount.

In preparation for distillation the petals are separated from the sepals and are covered with water in the still. The contents of the still are heated by means of coils of superheated steam. The oil which comes over with the steam is separated and the water is sold as orange-flower water.

Although this industry is of greatest importance in France, a small amount of oil of equal perfume value is prepared in Yunis and Algeria. The chief Yunisian center is the district of Nabeul. This district produces 60,000 kilos of flowers annually. The oil is distilled by Arabs, many of whom have but small stills which hold about 3 kilos.

The industry is also being well developed in Malaga.

Properties.—The oil of neroli of commerce is a yellowish, slightly fluorescent liquid, which becomes brownish red when exposed to light, of an intensive, highly pleasant odor reminding of orange blossoms, and a bitter aromatic taste. Its specific gravity is 0.870–0.880. The oil is soluble in 1½–2 volumes of 80 per cent alcohol. On the further addition of alcohol the liquid becomes turbid, and on standing crystalline flakes consisting of paraffin collect on the surface. The alcoholic solution of neroli oil distinguishes itself by a beautiful violet-blue fluorescence, which becomes especially prominent when some alcohol is poured in a layer above the oil.

On cooling strongly, the oil becomes turbid on account of the separation of paraffin. At times it even solidifies to a butter-like mass.

The saponification number of good oils lies between 20 and 52, corresponding to an amount of 7–18 per cent of linalyl acetate. Oils with a saponification number higher than 55 are suspicious.

In order to ascertain the properties of oils which were undoubtedly genuine, fresh orange blossoms which were partly preserved with salt, partly with sea water, for transportation, were distilled by the firm of Schimmel & Co.[1] and about 0.1 per cent of oil obtained which possessed properties given in Table XXV.

TABLE XXV

No.	Specific Gravity	a_D	Saponification No.	Behavior in a Freezing Mixture
1.....	0.887	Inactive	41	Solidifies to a butter-like mass
2.....	0.881	.....	36	Viscous, but not becoming solid
3.....	0.876	−0°52′	21	
4.....	0.872	−0°40′	21	

The rotatory power of No. 2 could not be determined on account of its dark color. Nos. 3 and 4 are distillates of the same shipment of blossoms. No. 4 consists only of the oil which separated directly in the receiver on distillation. Its preparation corresponds to the method usually employed in Southern France, where orange blossom oil is obtained as a by-product in the manufacture of orange blossom water. No. 3 is a normal product, i.e., a mixture of oil separating at once and that obtained by cohobation from water. The oils obtained by these two methods differ but slightly.

Of still greater importance for the determination of the constants of pure commercial oils than these experiments with preserved blossoms are the distillations of fresh material by Charabot and Pillet in Southern France. The oils distilled in May, 1898, in Cannes and Antibes behave as follows: The specific gravity was between 0.8720 and 0.8757, the angle of rotation, a_D, between −1.420 and −4.06°. One-tenth part of the oil dissolved in 1.3 to 1.6 parts of 80 per cent alcohol at 20. The amount of ester ($C_{10}H_{17}OCOH_3$) present was 13.4–18.0 per cent.

Some interesting quantitative distillations were made by Jean Gras in Cannes during the harvest of 1899. Thirty samples were distilled at different periods throughout the harvest. The yield increased as the season advanced, from 0.80 to 1.23 per cent. Schimmel & Co.[2] investigated twenty-five of the thirty samples. No marked differences were noted. The specific gravity varied from 0.873–0.877 at 15°, saponification No. 35.3–44.8, a_D −3°22′ to −5°24′ at 20°. All the oils were soluble in one and one-half and more parts of 80 per cent alcohol.

With few exceptions, the following oils have been examined in the laboratory of Schimmel & Co. The number in parentheses behind the geographic designation indicates the number of samples examined.

[1] *Report of Schimmel & Co.* (October, 1891), p. 26; (October, 1894), p. 40.

[2] *Report of Schimmel & Co.* (October, 1899), p. 42.

SPAIN (7)

$d_{15°}$ 0.870 to 0.885; a_D +9°30′ to +29°; $n_{D20°}$ 1.4705 to 1.4720; acid value 0.7 to 2.0; ester value 18 to 47, methyl anthranilate content 0.45 to 0.5 per cent.[1]

CALABRIA AND SICILY (11)

$d_{15°}$ 0.860 to 0.924; a_D +2°54′ to +56°30′; $n_{D20°}$ 1.468 to 1.474; acid value 0.3 to 1.0; ester value 6 to 127, methyl anthranilate content (1 determination) 0.22 per cent.

VENEZUELA (2)

$d_{15°}$ 0.884 to 0.887; a_D —0°55′ to —1°54′; $n_{D20°}$ 1.463 to 1.465; acid value 1.3 to 1.9; ester value 96 to 102.

PARAGUAY (1)

$d_{15°}$ 0.9076; a_D +0°25′; acid value 6.0; ester value 72.5.

MAYOTTE (1)

$d_{15°}$ 0.8562; a_D +46°2′; $n_{D20°}$ 1.4705; ester value 4.6.

ALGERIA

$d_{15°}$ 0.8723 to 0.8768; a_D +5°42′ to +6°6′; saponification value 72 to 91 (Chapus).

SYRIA (1)

$d_{15°}$ 0.8758; a_D 1°6′; saponification value 51.5.[2]

Composition.—Neroli oil is of special interest to the perfume chemist because it is the first oil in which there has been found a nitrogenous substance of great fragrance. Inasmuch as this valuable oil is indispensable to the perfumer, it has recently been subjected to repeated scientific investigation. As a result the presence of a considerable number of substances has been established.

The following compilation of constituents pertains to the ordinary neroli oil obtained by steam distillation.

l-α-Pinene (melting-point of pinene nitrolbenzylamine 122° to 123°.)[3]

l-Camphene. Upon treating fraction 168° to 170° with glacial acetic acid–sulphuric acid, H. Walbaum and O. Hüthig[3] obtained *iso*borneol which, however, melted at 195° instead of at 212°. Neither did A. Hesse and O. Zeitschel (1902) succeed in raising the melting-point beyond 200° although they purified the *iso*borneol through its phthalic acid ester.

Dipentene was identified in fraction 175° to 179° (a_D —1°6′) by means of its tetrabromide (melting-point 125°).[3] Previously F. Tiemann and F. W. Semmler had obtained a tetrabromide melting at 105° from fraction 75° (15 mm.) and had concluded the presence of limonene. Ap-

[1] *Ibid.* (October, 1903), p. 77.

[2] *Report of Roure-Bertrand fils* (April, 1911), p. 26.

[3] *Report of Schimmel & Co.* (October, 1902), pp. 54–57; also *Journal für praktische Chemie,* Vol. LXVII, Series 2 (1903), pp. 315–25.

parently they did not examine the optical rotation of the fraction, hence it may be presumed that the tetrabromide melting per chance at 105° was an impure dipentene tetrabromide. If this explanation is rejected, it must be assumed that the neroli oil in question was adulterated with orange oil, for pure oils yield fractions with but a slight rotation from which limonene tetrabromide cannot be obtained directly.

Decylic Aldehyde. From fraction 70° to 82° (7 to 8 mm.) shaking with bisulphite separated a solid compound which, when decomposed with alkali carbonate, developed the odor of decylic aldehyde.[1] Inasmuch as characteristic derivatives of this aldehyde have not been prepared, its presence has not yet been demonstrated. Its presence may, however, be regarded as probable since it occurs in the closely related orange oil.

l-Linalool had first been found in the oil by Tiemann and Semmler. Its presence was definitely proved by Walbaum and Hüthig[2] who prepared its phenylurethane melting at 65°. According to Hesse and Zeitschel (1901) the oil contains about 30 per cent of linalool, partly combined with acids.

l-Linalyl Acetate. According to Tiemann and Semmler fraction 97° to 104° (15 mm.; $d_{D20°}$ 0.8972) consists of linalyl acetate. When boiled with potassium hydrochloride, it was broken up into acetic acid and linalool. The presence of this ester was proved a second time by Hesse and Zeitschel (1901) who assumed that the oil examined by Tiemann and Semmler was largely adulterated with petitgrain oil. This assumption was not correct as demonstrated in detail by Walbaum and Hüthig.

Phenyl Ethyl Alcohol. This alcohol having been found by Hesse and Zeitschel in the oil extracted from the orange flower water, its presence in the oil proper was demonstrated by Walbaum and Hüthig (oxidation to phenyl acetic acid).

α-Terpineol (melting-point above 33°; melting-point of terpinyl phenyl urethane 112°)[3] (Hesse and Zeitschel, 1902).

Nerol. This alcohol, previously unknown, was discovered by Hesse and Zeitschel (1902) in neroli oil. Its boiling-point is somewhat lower than that of geraniol, but it does not combine with calcium chloride, hence can be separated from geraniol by this means. Its diphenyl urethane, however, does not melt at 73° to 75° as stated by Hesse and Zeitschel, but at 52° to 53°. Nerol is contained in the oil both free and as acetate.

Geraniol was first found in the oil by Tiemann and Semmler, but its presence was first definitely established by Hesse and Zeitschel who oxidized it to citral (melting-point of citrylidene cyanacetic acid 122°).

Jasmone. The presence in neroli oil of this ketone, first found by A. Hesse in jasmin oil, is probable, since the corresponding fraction yielded a semicarbazone melting at 200° to 204°.[4]

[1] *Report of Schimmel & Co.* (October, 1902), pp. 54–58. Also *Journal für praktische Chemie,* Vol. LXVII, Series 2 (1903), pp. 315–25.

[2] *Ibid.*

[3] *Ibid.*

[4] *Report of Schimmel & Co.* (April, 1903), p. 55.

Nerolidol. As found by Hesse and Zeitschel, the high boiling fractions contain a hitherto unknown sesquiterpene alcohol $C_{15}H_{26}O$, nerolidol. It is identical with peruviol and is characterized by a phenyl urethane melting at 37° to 38°, the formation of which, however, requires several weeks' standing of the alcohol with the reagent.[1]

Farnesol, which has a still higher boiling-point than nerolidol, was isolated by Schimmel & Co.[2] by treating fraction 127° (4 to 5 mm.) with phthalic acid anhydride. It was identified by means of its constants and by its conversion into farnesal (melting-point of semicarbazone 127° to 132° in place of 133° to 135°).[3]

Paraffin. The stearoptene of orange flower oil, also known as neroli camphor or aurade, was first found by Boullay. It is a paraffin which occurs in almost all flower oils and, when pure, is completely odorless and tasteless. It melts at 55°.[4]

Acids. In addition to the acetic acid already mentioned, neroli oil contains phenyl acetic acid[5] (Hesse and Zeitschel, 1902) which is found in larger amounts in the oil shaken out of the aqueous distillate, benzoic acid,[6] also traces of palmitic acid (Hesse and Zeitschel, 1902). All of these acids presumably exist in the oil as esters.

Phenols are present, but only in traces (Hesse and Zeitschel, 1902).

Anthranilic acid methyl ester. The most important rôle in the formation of the orange flower perfume is played by the small amount of anthranilic acid methyl ester, which was found in the oil in 1894 in the laboratory of Schimmel & Co.[7] It is the presence of this substance that causes the fluorescence of the oil. Anthranilic acid methyl ester $NH_2 \cdot C_6H_4 \cdot COOCH_3$ boils at 132° under 14 mm. pressure, melts at 25°, and while in the liquid condition at 15° has a specific gravity of 1.168. In the undiluted condition its odor is unpleasant. Only when greatly diluted does its odor remind of the fragrance of orange blossoms.

Several weeks after the *Report of Schimmel & Co.* and with it the report of Walbaum had been issued, there was published a paper by E. and H. Erdmann (1899) who claimed the scientific priority of the discovery of the ester in neroli oil.

After a rejoinder by Walbaum (1899), the Erdmanns (1900) claimed to prove their scientific priority by a German application for letters patent, E. 5958, in which the occurrence of anthranilic acid methyl ester in neroli oil is mentioned without, however, producing analytical proof. These let-

[1] *Ibid.* (1914), p. 72.

[2] *Ibid.*

[3] Cf. M. Kerschbaum, *Berichte der deutschen chemischen Gesellschaft,* XLVI (1913), 1732.

[4] Flückiger and Hanbury, *Pharmacographia,* p. 127 (2d ed.). London, 1879. Also E. and H. Erdmann, *Berichte der deutschen chemischen Gesellschaft,* XXXII (1899), 1214 footnote.

[5] *Report of Schimmel & Co.* (October, 1902), pp. 54–58. Also *Journal für praktische Chemie,* Vol. LXVII, Series 2 (1903), pp. 315–25.

[6] *Ibid.*

[7] *Report of Schimmel & Co.* (April, 1899), p. 32. Also H. Walbaum, *Journal für praktische Chemie,* Vol. LIX, Series 2 (1899), p. 350.

(Hill: The Princesse des Ursins)

MARIE DE LA TREMOUILLE (1635-1722), PRINCESS OF NEROLI, PRINCESS OF CHALAIS, DUCHESS OF BRACCIANO.

She is reported to have popularized orange flower perfume which has been named, after her, Oil of Neroli.

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ters patent were published July 5, 1900, hence fifteen months after the publication of Walbaum's first report. It thus becomes apparent that Walbaum's report was made public sooner than any of the communications by the Messrs. Erdmann.

Indol, likewise an important constituent of the oil, was first found by Engels in neroli pomade, later by Hesse and Zeitschel in the oil itself.

Pyrrol and pyrrol derivatives, found by Erdmann (1899) in neroli oil, do not, according to Schimmel & Co.[1] and Hesse and Zeitschel, appear to occur in genuine, unadulterated neroli oil. Probably the appearance of the pyrrol reaction (cherry-red coloration of a pine shaving moistened with hydrochloric acid when exposed to the vapors of the first fraction) may be attributed to an adulteration with petitgrain oil.

At the close of their second contribution on neroli oil, Hesse and Zeitschel presented a compilation of the constituents of the oil with approximate amounts. In somewhat modified form, in which the more recent investigations are considered, it is reproduced in Table XXVI.

TABLE XXVI

COMPOSITION OF NEROLI OIL

Constituents		Approximate Amount in Per Cent
Hydrocarbons 35 per cent	1. Pinene	35
	2. Camphene	
	3. Dipentene	
	4. Paraffin C_{27}	
Terpene alcohols and their acetates 47 per cent	5. *l*-Linalool	30
	6. *l*-Linalyl acetate	7
	7. *d*-Terpineol	2
	8 and 9. Geraniol + Nerol	4
	10 and 11. Geranyl acetate + Neryl acetate	4
Sesquiterpene derivatives 6 per cent	12. *d*-Nerolidol	6
Nitrogenous compounds 0.7 per cent	13. Anthranilic acid methyl ester	0.6
	14. Indol	less than 0.1
Acids and phenols 0.1 per cent	15. Acetic acid	—
	16. Palmitic acid	—
Other constituents, resinous products and loss	Decylic aldehyde (?) and esters of phenylacetic acid and benzoic acid, jasmone and farnesol	11.2

[1] *Report of Schimmel & Co.* (October, 1902), p. 54.

In the orange blossom water oil all of the above-mentioned constituents are likewise found, but in different ratios. Those substances which are more soluble in water, such as the alcohols and anthranilic acid methyl ester, exist in larger percentage in the water oil than in the neroli oil. The more difficultly soluble constituents, such as the esters of the terpene alcohols, are present in smaller amounts. The water oil possibly also contains phenyl acetonitrile, likewise a nitrogenous substance melting at 159° (Hesse and Zeitschel, 1902).

The orange blossom extract oil, according to Schimmel & Co.[1] contains, in addition to the substances found in the distilled oil, the following substances: traces of benzaldehyde (melting-point of semicarbazone 214°); a basic substance, with a decided odor of nicotine, that boils above 110° (6 mm.); and a nitrogenous substance which, upon saponification of the oil, is hydrolyzed to ammonia and phenyl acetic acid and which, in all probability, may be regarded as the nitrile of phenyl acetic acid. The nitrogenous substance, melting at 150° which had been found by Hesse and Zeitschel in the water oil, has also been obtained from the extract oil. Finally, it contains a ketone with the odor of jasmine, presumably jasmone (melting-point of semicarbazone 204° to 205°).

Examination.—The most common and most dangerous adulterants are the oils of bergamot and petitgrain. As these for the greater part possess the same constituents as oil of neroli—linalool and linalyl acetate—the detection of small amounts is impossible. Larger additions cause an increase in the specific gravity and the amount of esters, which in pure neroli oil is 7–24 per cent (saponification No. 20–69) in bergamot oil 34–45 per cent (saponification No. 100–130), in petitgrain oil 38–85 per cent.

Orange flower oils which show a saponification number higher than 70 are therefore rejected as suspicious.

The property of neroli oil to separate paraffin in a freezing mixture has been employed as a test, which is not wholly irrational, as the addition of paraffin free oils might decrease the relative amount of paraffin to such an extent that a separation no longer takes place on cooling. It must, however, be remembered in employing this test that some unadulterated oils may in certain cases be poor in paraffin. When, for instance, at the time of harvest a large amount of blossoms is to be quickly distilled, it happens that the distillation is not carried on to its complete exhaustion and that a smaller amount of the difficultly volatile paraffin gets into the oil. For the rest it is necessary in testing to depend on the comparison of the physical properties with those of good oils, especially of the odor.

OIL OF NEROLI PORTUGAL

Oil of sweet orange blossom, *Neroli Portugal,* i.e., the oil distilled from the blossoms of the sweet orange does not occur at all in commerce in a pure state. The goods sold under this designation are always a mixture of different aurantiaceous oils.

An oil distilled in Germany from the fresh blossoms of the sweet orange had entirely different properties from that procured from Southern

[1] *Report of Schimmel & Co.* (October, 1903), p. 49.

France.[1] The blossoms used for the distillation were transported from Southern Spain in iron casks from which the air was pumped after filling.

Properties.—The amount of oil obtained was 0.154 per cent, having the specific gravity 0.893 at 15° and the angle of rotation α_D +16°8′.

An oil[2] distilled in Spain revealed the following properties: $d_{15°}$ 0.8571; α_D +42°47′; $n_{D20°}$ 1.47274; acid value 1.6; ester value 6.8; insoluble in 80 per cent alcohol, readily soluble in 90 per cent alcohol with fluorescence and the separation of traces of paraffin.

Another oil from the same source examined by Schimmel & Co. had the following properties: $d_{15°}$ 0.8746; α_D +43°22′; $n_{D20°}$ 1.47450; acid value 3.7; ester value 16.7; insoluble in 10 volumes of 80 per cent alcohol, soluble in 0.3 volume of 90 per cent alcohol, from 2.5 volumes on opalescence is produced.

The properties of an Algerian oil are recorded by A. Chapus: $d_{15°}$ 0.8731; α_D +26°15′; ester content, computed as linalyl acetate, 34.18 per cent.

For scientific purposes an oil was prepared by E. Theulier in Southern France. The oil obtained by simple distillation without cohobation was dark yellow in color. Its odor did not remind of that of ordinary neroli oil. Its specific gravity was 0.860 at 23°, its angle of rotation +29°30′, the ester content 6.35 per cent. With 90 per cent alcohol the oil produced a silky turbidity. In the cold it separated paraffin melting at 55°.

An oil sent to Schimmel & Co.[3] from Southern France had the following properties: $d_{15°}$ 0.8686; α_D+45°16′; $n_{D20°}$ 1.47352; acid value 1.8; ester value 16.7; soluble in 0.5 volume of 90 per cent alcohol, the addition of more than 5 volumes produce produced opalescence.

Composition.—The oil examined by Theulier boiled between 160° and 233° and appeared to contain appreciable amounts of the higher terpenes. *d*-Camphene was identified by means of *iso*borneol melting at 212°, limonene by means of its tetrabromide melting at 105°, and *d*-linalool by means of Doebner's compound of citral melting at 198.5° which had been obtained upon oxidation of the linalool fraction. Those portions of the oil boiling above linalool were not examined. Anthranilic acid methyl ester was not contained in the oil. However, this ester was found to the extent of 0.3 per cent in a Spanish oil and was identified by means of its benzoyl derivative (melting-point 100° to 102°) and by means of its picrate (melting-point 105° to 106°).

ORANGE FLOWER PERFUME

Orange flower perfume cannot be obtained best by steam distillation. In order to prepare the substances which impart to them their fragrant odor, other methods are employed. The volatile oils may be extracted either with volatile solvents or with fat, or they may be allowed to be absorbed by fat.

Hence a distinction is made as in the oil from citrus rind between:

[1] *Report of Schimmel & Co.* (October, 1889), p. 38.
[2] *Report of Schimmel & Co.* (October, 1903), p. 77.
[3] *Ibid.* (April, 1910), p. 79.

(1) extraction with volatile solvents; (2) extraction with non-volatile solvents, i.e., fats: (*a*) without the aid of heat, enfleurage, (*b*) with the aid of heat, maceration. Which of these methods is best adapted to the extraction of the perfume of a particular flower has been determined in Southern France by long years of experience.

The extraction of orange blossoms has thus been restricted to the use of volatile solvents and maceration. They can be treated equally well either with volatile solvents or with warm fats.

The perfume of the orange flower is ready made and is not manufactured after the flower has been separated from the plant as is the case with the jasmine and tuberose.

According to Hesse and Zeitschel, 1,000 kilos of orange blossoms yield only 100 gm. of volatile oil when submitted to the enfleurage process, whereas maceration yields 400 gm. and distillation with steam 1,200 gm. of oil, of which, however, about 400 gm. are dissolved in the aqueous distillate.

EXTRACTION WITH VOLATILE SOLVENTS

A more detailed study of the extraction of flowers with volatile solvents was made by Millon in Algiers. In addition to ether he recommended chloroform, carbon disulphide, wood alcohol, and the low-boiling fractions of benzin.

Millon placed the flowers into a percolator (*appareil à déplacement*) covered them with ether and renewed the menstrum after ten to twenty minutes. The extract, obtained after evaporation of the ether, he kept in open containers because he thought that the air acted favorably on the odoriferous principle. This, however, was a deception. Unless the solvent is carefully removed with the aid of a vacuum, mere traces of it can be detected if the extract is kept in closed containers. Millon was not ignorant of the fact that the greater part of the extract consists of vegetable wax which is well-nigh insoluble in alcohol. Hence he determined the amount of odoriferous substances by ascertaining the difference in weight of the extract before and after treatment with alcohol.

The substitution of petroleum ether for ether, a practice now in common use, was suggested by Hirzel of Leipzig. His apparatus constructed for this purpose was patented as early as 1864 in France, England, Austria, and several of the German states. The problem of utilizing on a technical scale the extraction with ether, carbon disulphide, chloroform, and petroleum ether was developed about the same time by Piver. The use of methyl chloride as a solvent was recommended by C. Vincent.

In the early seventies, Roure devised a method for the preparation of the so-called *essences concrètes,* concentrated alcoholic perfumes, obtained by extraction. These were exhibited at the Vienna Exposition in 1873. A very complicated apparatus was patented by Naudin in 1875. This permitted of the vacuum distillation of the solvent charged with the perfume.

However, it is only during the last twenty-five to thirty years that the method of floral extraction with volatile solvents has found industrial application. It was at the time that Massignon in Cannes erected a battery of extraction apparatus similar to the diffusion apparatus employed in sugar

factories. The solvent saturated with perfume was evaporated in a vacuum still. As a menstrum Massignon first used ether, carbon disulphide, methyl chloride, and benzene. Finally he arrived at the conclusion that a petroleum ether of the specific gravity 0.650 was best suited. Later Massignon sold his factory and his patents to Leon Chiris. Gradually other factories were equipped with extraction batteries.

Practically the process of extraction with volatile solvents resolves itself into four steps: (*a*) selection and purification of the solvent; (*b*) the systematic extraction of the flowers; (*c*) evaporation of the solvent and production of the vegetable wax saturated with perfume (*cire parfumée*); (*d*) recovery of the solvent.

Selection and purification of the solvent.—The solvent most commonly used is petroleum ether of a specific gravity 0.650 (15°). It is purified by consecutive treatment with sulphuric acid and caustic soda, washing with water, and rectification with the aid of a column in a still over solid paraffin for the purpose of removing the lighter as well as the heavier fractions. Less frequently benzene is used since it has the disadvantage of yielding a highly colored extract. Carbon disulphide is not serviceable since the extract always retains some of the disagreeable odor of the solvent. Neither has carbon tetrachloride maintained itself. The high price of ether stands in the way of its general use.

The systematic extraction of the flowers.—The extractors of the mounted extraction batteries are cylindrical vessels, varying in size, but usually of about 500-liter capacity. They contain three or four low cylinders made of wire gauze or of perforated tin, one placed over the other. The extractors are air-tight and sealed with a removable cover. The batteries are mounted in one of several ways: either the extractors are all on a level in a circle or a row or in two tiers one over the other. With the aid of a pump, the solvent can be passed from one extractor to another.

As a rule, three or four extractions are made within twenty-four hours. Hence the menstrum remains in contact with the flowers from six to eight hours. Then the flowers are replaced by fresh ones. However, during the height of the harvest the flowers in the extractors are replaced every eight or even every four or five hours. This hastening of the process, however, results in an imperfect extraction.

Each batch of flowers is usually extracted three times, more rarely twice or four times. For the third (or last) extraction fresh petroleum ether is used, for the second, that which served for a former third extraction, and for the first extraction (i.e., for fresh flowers) the menstrum which has once served for a second and once for a third extraction. The percolate of each extraction is collected in a separate receiver.

How many times the same batch of flowers is to be extracted depends upon the nature of the flowers to be examined and also on the views of the manufacturer. A difference of opinion exists as to how often the same petroleum ether can be used before it is to be recovered by distillation.

In order to increase the yield, the extractors have been so constructed in several instances as to enable their being warmed. This has resulted in a larger yield of wax but not of odoriferous constituents.

Evaporation of the solvent.—The manufacturer operates one or several stills under ordinary pressure or in vacuum. As a rule the bulk of the solvent is recovered in a large still under atmospheric pressure until the temperature has reached a point that would prove detrimental to the fineness of the perfume. The distillation is then continued in a vacuum still and finally concluded in a glass flask.

The last traces of solvent are removed by passing small amounts of alcohol into the molten wax thus causing a violent ebullition.

The floral extracts thus obtained are designated "concrete oils" (*essences concrètes*). The alcoholic extracts prepared from these, according to the method described below, are known as "floral extracts" (*extraits aux fleurs*); the pure oils remaining after the removal of the alcohol as "quintescences."

Recovery of the solvent.—On account of the expense of the solvent, suitable devices are provided to prevent loss. Hence long and well-cooled spirals are used to condense the vapors from the stills, the extractors, and the reservoirs. The ejectors of the vacuum pump must also be provided with an efficient condenser. If the process is conducted without a vacuum, the petroleum ether losses are less, but evaporation under atmospheric pressure, as already pointed out, results in an impairment of the fragrance.

The solvent adhering to the flowers after their extraction is recovered by passing steam through the extractors which, for this purpose, are connected with the condensers; or by transferring the flowers to a still from which the solvent is recovered by steam.

a) *Yield.*—The yield varies greatly according to the solvent and temperature employed, also according to the duration of the extraction.

At ordinary temperature, petroleum ether yields for every kilo of orange flowers from 2.0 to 4.0 gm. of concrete oils.

b) *Removal of the plant wax from the concrete oils.*—For this purpose the *essences concrètes,* i.e., the extracts obtained by percolation and subsequent evaporation of the solvent, are shaken for several days with strong alcohol, preferably in shaking machines (*batteuses*). The alcoholic solution, after being separated from the insoluble wax, is cooled for some time to 0°. This causes the separation of the dissolved wax, which is removed by filtration. To the alcoholic filtrate a solution of common salt is added, and the perfume, which has risen to the surface, is separated. If necessary, the last traces of alcohol are removed with the aid of a vacuum.

Inasmuch as the plant wax when shaken with alcohol agglutinates to a magma from which the perfume is extracted with difficulty, Massignon has suggested to mix it with a very hard and odorless mineral wax, thus yielding a mass that can be broken up in a mortar. The particles then remain suspended in the alcohol and are more readily extracted by it.

EXTRACTION WITH NON-VOLATILE SOLVENTS WITH THE AID OF HEAT: INFUSION, MACERATION OR "ENFLEURAGE À CHAUD"

The extraction by fixed solvents is, of course, obtained by the means of fats. It is a rather ancient method of extracting perfumes. The fats used are those of pork and beef, or a mixture of them.

This process of extraction is used in numerous cases, varied only according to the flowers being dealt with. Some of these yield the whole amount of their perfume at the time of the extraction; others are able to produce an extra quantity of perfume under the conditions, and the period of association with the fatty absorbent is extended. In the former case the extraction is performed by "hot maceration" (*macération à chaud*), in the latter by "enfleurage." The principle of this extraction is, in both cases, intimate contact between the flowers and the fat. The odoriferous products then leave the vegetable cells of the flower to incorporate with the fat in which they are absorbed.

These fats must, of course, be of A-1 quality, and perfectly odorless. Before using them they are subjected to an extremely careful purification, the object of which is to free them from all putrescible substances. The preparation of these fats takes place in February and March, in order to have the refined material—the *corps,* as it is called—ready to be used at the time of the first deliveries of flowers (violets). After olfactory examination, the fats are crushed, melted, and filtered. The fat is then very slowly cooled, while being constantly mashed. This operation is called *lissage.* Before being employed, these *corps,* contained in very clean "piles," are stored in cool cellars, connected with the various floors of the factory, where the making of pomades takes place.

The preparation of pomades is a very delicate one, requiring much experience from the foreman in charge who is called *contremaître pommadier.*

Maceration.—this operation is made by the hot process. It is used for the extraction of the perfume of rose, violet, orange flower, and cassia.

The infusing material is prepared in the laboratory, and consists of lard, to which has been added beef fat, deprived of all impurities, and washed with a solution of alum; this second fat is necessary to impart the required degree of firmness. This compound grease, called the *corp préparé,* is placed in a basin which is warmed on a water bath. The operation is carefully watched, and the heat regulated according to the thermometer, so as to avoid overheating.

Immediately over this department is the weighing-room, where the flowers are piled in heaps. By the aid of long sacks the workman pours a weighed quantity into each vat through an opening in the floor just above it. Another employee mixes together the flowers and grease with a stirrer. The heat (50° to 70°) then bursts the cells containing the essential oil, and the floral odor is absorbed by the warm fat. After half an hour the contents of the vat are thrown onto a great sieve, which retains the flowers and allows the grease to run through. The recovered, partly aromatized fat is treated with fresh flowers. This is repeated ten to fifteen times[1] until the fat has acquired the desired strength as to odor. There remains the fat held by the flowers which have been kept back by the sieve. These are filled without delay into sacks. These are then placed in a hydraulic press which separates the last trace of perfumed fat from the flowers.

[1]According to Labbe, the average is six to eight times (H. Labbe, *Essais des Huiles essentielles,* p. 11. Paris).

The fineness of the aroma of the pomade is inverse to the time of exposure of the flowers to the action of the fat. If prolonged unduly, other odoriferous substances that interfere with the quality of the perfume are also absorbed.

The floral extracts obtained by maceration are known by the same names as those obtained by the enfleurage process and are treated in like manner for the separation of the volatile oil. Here also the recovered fat, the *corps équisé*, is not used again in the perfume factory but finds its way into the soap industry.

LIME FLOWER OIL

Parry examined an oil distilled from the flowers of the Italian lime tree (*Citrus limetta*), and found it to have the following characteristics: Specific gravity 0.870; optical rotation $+21°30'$; it contained linalool and methyl anthranilate.

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CHAPTER IX

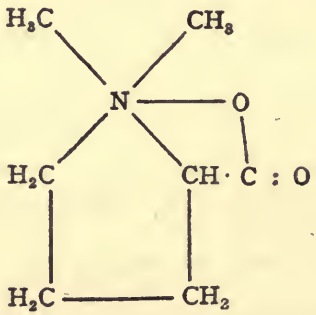
PRODUCTS FROM THE LEAVES

Petitgrain oil which is obtained by distillation from the leaves of *Citrus Aurantium* is dealt with in chapter x, as this oil is also obtained from the stems of the plant.

Besides volatile oils citrus leaves, especially those of oranges, contain a soporific substance and an alkaloid.

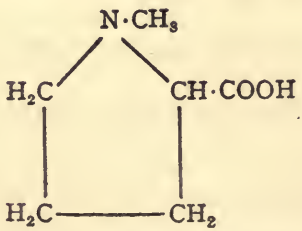
Hoffman–La Roche & Co. have recently succeeded in preparing from orange leaves a solid substance which has hypnotic properties. In the manufacture of the hypnotic substance an aqueous extract of the leaves is evaporated at a low temperature to a syrupy consistency. Alcohol is added to the residue.

An alkaloid known as stachydrin, methylbetain of hygrin acid, or dimethylbetain of α-prolin, whose structural formula is as follows:



$= C_7H_{13}NO_2$

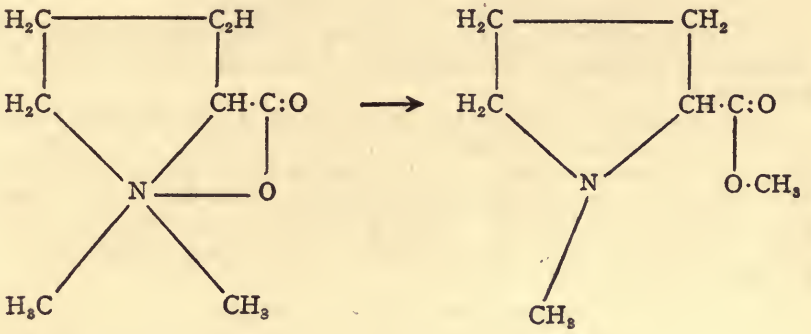
has been found in the leaves of *Citrus aurantium,* as well as in the tubers of *Stachys tuberifera* (E. Jahns). This alkaloid has a sweet taste and



= Hygrin acid or
l-methyltetrahydropyrrole.

separates in optically inactive crystals from a mixture of alcohol and ether. These crystals are colorless, hygroscopic, and contain one molecule of water of crystallization. By heating at 100°C. this water is given off. When the hydrochloride of the ethyl ester of the substance is decomposed

by HCl gas *l*-methyltetrahydropyrrole (2-carboxylic acid) is formed. Decomposition with potassium hydroxide yields dimethylamine and thereby evidence is given for the foregoing constitutional formula. This formula is further established by synthesis from the treatment of the methyl ester of the substance with methyl iodide and then with a silver oxide.



Methyl betain of Hygrin acid — by distillation to isomeric form — Methyl ester of Hygrin acid

The experimenters considered that according to the constitution of stachydrin it might be formed as a decomposition product of albumen. One support of this hypothesis lies in the fact that in the sap of the starchy tubers examined stachydrin was accompanied by glutamin, tyrosin, and arginin which are products formed when albumen decomposes.

OIL OF BERGAMOT LEAVES

According to S. Gullì the distillation of bergamot leaves *Citrus Bergamia* Risso, is conducted on a restricted scale. It is practiced between February and April when the trees are cleaned and trimmed. The yield is small (100 kg. of leaves yield but 150 gm. oil) and the entire output for a year is said not to exceed 20 to 25 kg. The pure oil has a specific gravity of about 0.870 to 0.873, an optical rotation of +25° to +26°. It is soluble in an equal volume of 90 per cent alcohol. It contains about 32 to 34 per cent of esters, computed as linalyl acetate, some of which, however, is methyl anthranilate.

The oil is rarely met with in a pure condition. Frequently the bergamot leaves are distilled with the addition of turpentine oil. Still more frequently the young plants of the bitter orange tree are admixed. Rind oils also are used freely as adulterants. However, the oil is not only adulterated itself, but it in turn is used for the adulteration of petitgrain oil and orange flower oil, both bitter and sweet.

OIL OF PAPEDA LEAVES (CITRUS HYSTRIX D. C.)

According to B. T. Brooks, the leaves of this group of Malayan citrus trees do not yield more than 0.08 per cent of volatile oil with the following properties: $d_{30°}^{30°}$ 0.9150; α_D —10.50°; $n_{D30°}$ 1.4650; saponification value 50.2. Its odor resembles that of the oil from grapefruit.

OIL OF LEAVES OF "CITRUS TRIFOLIATA"

A Chinese neroli oil, said to have been obtained from the leaves of *Poncirus trifoliata* Raf. (*Citrus trifoliata*, L.) has been described by Umney and Bennett.

The yellowish-brown oil had a peculiar sweetish odor, revealed a very faint blue fluorescence and had the following constants: $d_{15°}$ 0.850; α_D +35°; ester content 4.97 per cent, computed as linalyl acetate; total alcohol content 25.17 per cent, computed as linalool. According to the investigators the oil contains limonene, camphene, linalool, linalyl acetate, anthranilic acid methyl ester, and a paraffin. How these substances were identified is not stated.

OIL OF SWEET ORANGE LEAVES

Two oils (petitgrain Portugal) distilled in Southern France from the leaves of the sweet orange tree (*Citrus sinensis* Osbeck) had the following properties:[1] $d_{15°}$ 0.8602 and 0.8584; α_D +56°46′ and 53°52′. An Algerian oil was examined with the following results (Chapus): $d_{15°}$ 0.8705; α_D +21°33′; ester content, computed as linalyl acetate 21.6 per cent. The oil contains (Litterer) *d*-camphene (melting-point of *iso*borneol 212°), limonene (melting-point of tetrabromide 104°), linalool (?) citral, about 4 per cent (melting-point of naphthocinchoninic acid 197°) and geraniol, about 12 per cent (calcium chloride compound).

OIL OF GRAPEFRUIT LEAVES

According to Brooks (cited by Parry) the leaves of a variety of grapefruit (*Citrus grandis* Osbeck) growing in the Philippines, yields 1.7 per cent of an oil having the following characters:

Specific gravity at $\frac{30°}{30°}$	0.870
Optical rotation at 30°	+22.9°
Refractive index at 30°	1.4644
Ester number	10

It contains dipentane, 15 per cent of linalool, and 1 per cent of citral.

OIL OF LIME LEAVES

The leaves of the West Indian lime tree (*Citrus aurantifolia* Swingle) yield, according to Parry, on distillation, an oil which has the following characteristics:

Specific gravity	0.877–0.878
Optical rotation	+37°–38°
Acid value	3–5
Ester value	22–25
Aldehydes	43 per cent

[1] *Report of Roure-Bertrand fils* (October, 1904), p. 35; (October, 1910), p. 42.

OIL OF MANDARIN LEAVES

Production.—Upon distillation with water vapor, the leaves of the mandarin tree (*Citrus nobilis* var. *deliciosa* Swingle) yield from 0.2 to 0.35 per cent of volatile oil which in the receiver usually separates into a lighter and a heavier oil.

Properties.—A Spanish oil described by Schimmel[1] which had been obtained from Carcagente, was yellowish in color and showed a decided bluish fluorescence, $d_{15°}$ 1.0142; α_D +7°46′; ester value 216; soluble in 6 to 6.5 volumes of 80 per cent alcohol. The properties of an oil from Southern France[2] were $d_{15°}$ 1.005; α_D +7°19′; saponification value 159. Another oil from the same source[3] had $d_{15°}$ 1.0643; α_D +2°20′; saponification value 26.5.

The oil examined by Charabot (see under Composition) deviated the polarized light +6°40′; saponification value 160; content of methyl anthranilic acid methyl ester about 50 per cent.

Upon the distillation of 250 kg. of leaves in Grasse, Hesse obtained 618 gm. of light oil and 159 gm. of heavy oil. The former showed $d_{15°}$ 0.993; α_D +5°42′; saponification value 191; content of methyl anthranilic acid methyl ester 55.7 per cent. The heavy oil showed $d_{15°}$ 1.033; α_D +3°20′; saponification value 238; content of methyl anthranilic acid methyl ester 67.65 per cent. Both oils congealed in a freezing mixture. From the aqueous distillate an additional 80 gm. of oil were obtained that contained over 80 per cent of ester. The methyl anthranilic acid methyl ester content of the total oil was computed at 65 per cent. There were also found in this leaf oil a small amount of other esters, likewise a non-saponifiable base with an odor of nicotine.

Composition.—As shown by Charabot mandarin leaf oil consists principally of methyl anthranilic acid methyl ester.[4] It was isolated and identified according to the method employed by Walbaum in his investigation of mandarin oils. The melting-point of the ester was 19°. It was identified as methyl anthranilic acid methyl ester by elementary analysis and by the acid obtained upon saponification which melted at 179° and showed all of the properties of methyl anthranilic acid.

[1] *Report of Schimmel & Co.* (October, 1902), p. 83.

[2] *Ibid.* (April, 1902), p. 81.

[3] *Report of Roure-Bertrand fils* (October, 1910), p. 42.

[4] E. Charabot and G. Laloue (*Comptes Rendus,* CXXXVII [1903], 996. *Bulletin de la Société de Chimie,* Vol. XXXI, Series 3 [1904], p. 195) have made a study of the origin of the volatile oil, more particularly of the methyl anthranilic acid methyl ester, in the leaves and petioles of the mandarin tree. It was found that the formation of the volatile oils in the leaves is most active while their organs are young. Moreover, the leaves contain more oil than the petioles. Later the terpene content of the leaves is diminished whereas that of the petioles is increased. The water-soluble constituents (methyl anthranilic acid methyl ester) seem to accumulate in the leaves during the process of vegetation, the reverse being true of the petioles.

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CHAPTER X

PRODUCTS FROM THE STEMS

OIL OF PETITGRAIN

Origin and preparation.—Petitgrain oil is obtained from the leaves, twigs, and immature fruit of the bitter orange (*Citrus Aurantium* L.), by distillation with water. Formerly the oil was principally produced in Southern France, but toward the end of the seventies French colonists began the distillation in Paraguay. The poor quality of the oils there produced in the beginning improved in the course of the years to such an extent that the South American oil is now generally preferred on account of its greater reliability and uniformity to the often adulterated French product. The market for the Paraguay oil is Ascuncion[1]; the principal place of distillation is said to be the little town of Yaguaron.

Properties.—The odor of petitgrain oil is similar to that of neroli, but far less delicate, the taste is aromatic and somewhat bitter, the color yellowish. Its specific gravity is 0.886–0.900. It turns the polarized ray of light either slightly to the right or to the left; α_D $+5°$ to $-2°45'$. The oil is soluble to a clear solution in two parts of 80 per cent alcohol. The saponification number is 110—245=38—85 per cent of linalyl acetate.

Those oils with a lower specific gravity and a larger dextrorotation are mostly poorer in linalyl acetate and hence inferior.[2] Nevertheless, oils have been frequently observed which, in spite of the deviations mentioned, revealed a normal ester content. Thus for oils with from 37 to 46 per cent linalyl acetate content, the following constants have been observed: $d_{15°}$ as low as 0.883; and α_D $+5°10'$ to $+11°3'$. In isolated cases the oils differed from the normal only by a stronger dextrorotation (e.g., $d_{15°}$ 0.8907; α_D $+7°48'$; 39.7 per cent ester; yielded a turbid solution with about 5 volumes and more of 70 per cent alcohol, soluble in 1 volume and more of 80 per cent alcohol). Presumably these deviations are due to the selection of the crude material, though unfavorable climatic conditions may be accountable therefor.

Eight different petitgrain oils recently distilled from the leaves of the bitter orange by Charabot and Pillet in Cannes, had the following

[1]See Part II of this book.

[2]*Report of Schimmel & Co.* (October, 1910), p. 107.

properties: $d_{15°}$ 0.8910–0.8934; α_D −5°12′ to −6°15′. Soluble in 1–1.1 parts of 80 per cent alcohol. The amounts of ester varied from 51.5–69.6 per cent.

TABLE XXVII
PROPERTIES OF PETITGRAIN OILS OF VARIOUS SOURCES

Source	$d_{11°}$	α_D	Acid Value	Ester Value	Per Cent Ester
Calabria	0.8746	+18°	0.5	75.4	26.3
Spain	0.8849	+8°25′	...	81.7	28.6
Comores	0.8664	+42°45′	1.8	31.0	10.9
Jamaica	0.8846	−6°30′	...	82.0	28.7
West Indies	0.8531	+43°36′	1.2	6.1	2.1
South America*	0.887	+2°	...	....	36.5
Syria†	0.8857	−3°24′	...	....	27.1

*J. C. Umney and C. T. Bennett, *Pharmaceutical Journal*, LXXII (1904), 217.
†*Report of Roure-Bertrand fils* (April, 1911), p. 26.

The influence of climatic conditions on the formation and composition of petitgrain oils has been studied by Jeancard and Satie for the years 1901 to 1903.

Composition.—Pyrrol and furfurol. The vapors of the first distillate of the oil color a pine shaving, moistened with hydrochloric acid, cherry-red (H. and E. Erdmann), a reaction that indicates the presence of pyrrol derivatives.[1] Besides, the lowest fraction contains furfurol (color reaction with aniline hydrochloride).[2]

Camphene. When fraction 160° to 170° was treated with glacial acetic acid–sulphuric acid, the odor of *iso*borneol resulted. However, no crystals of this alcohol could be obtained.

β-Pinene. Upon oxidation of fraction 167° to 170° ($d_{15°}$ 0.8474; α_D −7°10′) with potassium permanganate in alkaline solution, a good yield of sodium nopinate, crystallizing in shining laminae, was obtained. Decomposed with sulphuric acid, it yielded nopinic acid melting at 126° to 127°. For further identification nopinic acid was converted into nopinone which condensed readily with benzaldehyde forming the benzylidene compound $C_9H_{12}O : CHC_6H_5$ melting at 107°.[3]

Dipentene and *Limonene.* Walbaum and Hüthig proved the presence of dipentene by means of its tetrabromide (melting-point 125°), whereas, according to Tiemann and Semmler, limonene is contained in the oil. Charabot and Pillet have found that the petitgrain oil distilled from the leaves only contains no limonene and that the *d*-limonene occasionally found in the oil is due to the small fruits.

[1]*Schimmel* (October, 1902), p. 69.
[2]*Ibid.*
[3]*Ibid.* (April, 1914), p. 83.

l-Linalool, which occurs both free and as ester, was first shown to be present by Tiemann and Semmler. This observation was later verified by Walbaum and Hüthig by means of the phenylurethane of the linalool melting at 65°, a compound previously unknown.

d-α-Terpineol. (Melting-point 34°; melting-point of phenylurethane 112° [Walbaum and Hüthig].)

Nerol. Von Soden and Zeitschel found about 2 per cent of this alcohol in petitgrain oil.

Geraniol is present both free and as acetate (Parry); melting-point of diphenyl-urethane 82°; analysis of the silver salt of the acid (Walbaum and Hüthig).

The highest boiling portions of petitgrain oil contain sesquiterpenes (Tiemann and Semmler) that have not been further investigated. The blue fluorescence of the oil is in all probability due to anthranilic acid methyl ester.[1] Upon shaking the fraction which boils in the neighborhood of 200° with dilute sulphuric acid, Walbaum and Hüthig obtained traces of an oil which had a strongly basic odor and which probably produces the characteristic petitgrain odor.

Adulteration and examination.—Petitgrain oil is adulterated with orange oil, lemon oil, and turpentine oil. These additions are readily recognized by the lowering of the specific gravity, decrease in the saponification number and the solubility, and finally by the change in rotatory power.

Of other adulterants that are more difficult of detection, the following have been observed: ethyl tartrate (Parry, 1909), oleic acid (Parry, 1909), also terpinyl acetate.[2]

A number of specimens of petitgrain oil have been found during the last few years, having a somewhat low ester value, and a high optical

TABLE XXVIII

	1	2	3	4
$d_{15°}$	0.9019	0.8968	0.8917	0.8005
α_D	+4°47′	+1°40′	+2°56′	−12°0′
Solubility	5 vol. and m. 70% alc. dilute sol. opal.	3 vol. and m. 70% alc.	1 vol. and m. 80% alc. dilute sol. opal.	Any vol. 90% alc.
Acid value	2.3	0.3	0.5	0.5
Ester value after 1 hour saponification with 10 c.c. N/2 alkali	111.2	112.4	136.8	84.0
Ester content (calc. as linalyl acetate)	38.9%	39.4%	47.9%	29.4%
Ester value after 2 hours saponification with 20 c.c. semi-normal alkali	119.3	121.8	138.5	89.0
Ester value after 1 hour saponification with 10 c.c. semi-normal alkali	102.3	99.7	133.5	80.5
Difference	17.0	22.1	5.0	8.5
Saponification value	113.5	112.7	128.4	.....
Acid value II	107.6	112.4	128.4	.....
Difference	5.9	0.3	8.9	.....
Terpinal acetate content about	9.0%	12.0%	.....	.....

[1] *Ibid.* (October, 1902), p. 68.

[2] *Report of Schimmel & Co.* (October, 1912), p. 92.

rotation. This is probably due to the more or less careless selections of the material to be distilled, in which some young fruits, more mature than usual, have been included. The ester value of such oils falls to 35 per cent, and the optical rotation rises to 19°. A sample of petitgrain oil, of authentic origin, distilled in Jamaica[1] has been found to have a rotation $-6°45'$.

Terpinyl acetate has recently been found as an adulterant of this oil. The results in Table XXVIII are obtained on the analysis of several samples of petitgrain oil so adulterated. The analyses are by Parry and by Schimmel.

PETITGRAIN CITRONNIER

By this name an oil is designated which is obtained now and then from the twigs, leaves, and unripe fruit of the lemon tree. Its odor is similar to that of the petitgrain oil, but the lemon-like odor accompanying it betrays the source of the oil. Its specific gravity is 0.868–0.874; a_D $+22°5'$ to $+34°12'$; saponification number 14.5–32.2. The odor, also the property of forming a crystalline compound with bisulphite solution caused the presence of citral to be suspected. In fact the citryl β-naphtho cinchoninic acid was obtained, and the presence of this aldehyde thereby proved.[2] This oil is not made in southern California although the territory looks promising especially as regards oil from lemon leaves and branches. There is an abundance of lemon prunings which at present are either burned up and their ashes used as fertilizer or they are cut up by machines to be left as humus in the orchards.

OIL FROM IMMATURE ORANGES

From the unripe bitter Sicilian orange, Haensel obtained upon distillation 0.712 per cent of oil (a_D about $+49°$), and from Spanish material 0.372 per cent (a_D about $+58°$). This oil contains appreciable amounts of a pyrrol derivative, for the vapors, even of the unfractionated oil, produce a bluish-red color on a pine shaving moistened with hydrochloric acid (Erdmann). The principal constituent of the oil is limonene (Haensel).

ORANGE AND LEMON WOOD

Orange and lemon wood is used for manicure sets, dentists' tools, wagon eveners, single-trees and neck yokes. For this purpose it has been found that young trees have greater strength than old and trees grown in windy sections are stronger and tougher than those grown in sheltered places. In California August and September, which are dry, are the best months for cutting the branches or felling the trees for this purpose. For the best results, the limbs are allowed to lie with the leaves on them for ten days after felling; much of the moisture is evaporated from the leaves. If treated in this manner, the wood will not check nor be damaged by insects.

One firm received an order for fifteen carloads of wood and paid the growers $10 per ton for logs 3 or more inches in diameter.[3]

[1] *Bull. Imp. Instit.* (1913), pp. 11, 437.
[2] *Report of Schimmel & Co.* (October, 1896), p. 59.
[3] *California Citrograph*, VII, No. 7 (May, 1921), 231, 256.

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